NATIONAL TECHNICAL UNIVERSITY OF ATHENS

School of Chemical Engineering

Department of Process Analysis & Plant Design

DIPLOMA THESIS

Investigation of electrostatic and interfacial phenomena on SiO_2 plates with the streaming potential technique

by

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June 2015

Acknowledgements

For the realization of this project I would like to thank first of all my professor Mr A. Boudouvis for the trust he showed me by giving me the opportunity to complete my diploma thesis under his supervision in cooperation with the CIRIMAT laboratory of the INP Toulouse in the framework of the ERASMUS program. I would also like to thank him for his time and precious advising during our collaboration.

Moreover I would like to thank Dr. C.Vahlas for accepting me in his team, for his time and advice whenever problems were arising as well as for his outermost support for making me feel an actual part of the University of Toulouse.

Moreover I would like to express my gratitude to Dr. Claire Tendero and Diane Samelor for being an active part of my project by helping me and answering my questions whenever needed.

I would also like to thank Mr Yannis Aviziotis who gave me great support during my first days at the University of Toulouse and shared his experience with me.

Finally I would like to thank all the members of the research team of the university along with Daniel Sandowski and Thomas Duguet who tried to do their best to help me with my experiments as well as for their confidence in me.

Contents

Διερεύνηση ηλεκτροστατικών και διεπιφανειακών φαινομένων σε πλακίδια SiO_2 με τη τεχνική του δυναμικού ροής

Εκτενής Περίληψη

Σε αυτή τη διπλωματική εργασία γίνεται διερεύνηση του υπολογισμού του ζ-δυναμικού (z-potential) πλακιδίων SiO_2 με σκοπό να κατανοηθεί καλύτερα η χρησιμότητα της τιμής αυτής αλλά και να διερευνηθούν οι πληροφορίες που μπορεί να δώσει για τις επιφάνειες των υλικών. Η αρχική μελέτη του ζ-δυναμικού έγινε στο πλαίσιο του ερευνητικού προγράμματος του εργαστηρίου CIRIMAT (Centre interuniversitaire de Recher et d'Ingenierie des Materieux) στο Πανεπιστήμιο της Τουλούζης (INP-Toulouse/CIRIMAT) με τελικό στόχο την διευκρίνηση των αλλαγών στην επιφάνεια πιεζοηλεκτρικών υλικών (PZT) ύστερα από ατμοσφαιρική εκκένωση πλάσματος.

Στην αρχή παρουσιάζεται μια θεωρητική ανασκόπηση των φαινομένων και της σχετικής θεωρίας. Το ζ-δυναμικό αναδεικνύεται ως ένα σημαντικό εργαλείο για την κατανόηση και τη μέτρηση της ενέργειας και της συμπεριφοράς των διεπιφανειακών συστημάτων υγρών-στερεών. Η «καρδιά» των φαινομένων είναι η διεπιφάνεια των δύο φάσεων, όπου οι φάσεις διασπείρονται η μια στην άλλη.

Το πρώτο βήμα για την κατανόηση της έννοιας του ζ-δυναμικού είναι η ερμηνεία του φαινομένου της διπλής στιβάδας που δημιουργείται στις επιφάνειες των στερεών όταν έρχονται σε επαφή με ένα υγρό. Είναι σημαντικό να εξηγηθεί και να κατανοηθούν οι μηχανισμοί γύρω από αυτή τη στιβάδα η οποία καθορίζε σε σημαντικό βαθμό τη συμπεριφορά των στερεών μέσα σε υγρά περιβάλλοντα.

Η διερεύνηση των φαινομένων στη συγκεκριμένη περιοχή, η οποία δεν υπερβαίνει μερικά nn σε διαστάσεις, είναι στο επίκεντρο θεωρητικής ανάλυσης. Οι δύο κύριες παράμετροι που επηρεάζουν και ελέγχουν τη συμπεριφορά του όλου συστήματος είναι η διεπιφανειακή χημεία και το ίδιο το περιβάλλον.

Για το ζ-δυναμικό αναφέρονται οι θεωρίες σχηματισμού και διάρθρωσης της διπλής στιβάδας. Αρχικά η θεωρία του Helmholtz, η οποία αποτελεί την πιο βασική προσέγγιση, υποθέτει 2 παράλληλες στιβάδες ιόντων. Στη συνέχεια αναφέρονται πιο σύνθετες θεωρίες οι οποίες λαμβάνουν υπόψη και επιμέρους φαινόμενα όπως τη χημική ρόφηση κτλ. Γίνεται σύγκριση των θεωριών και έπειτα διατυπώνονται βασικές εξισώσεις που συμπεριλαμβάνουν και οδηγούν στον υπολογισμό του ζ-δυναμικού.

Οι εξισώσεις αυτές βασίζονται στην θεώρηση ότι υπάρχει ένα ηλεκτρικό φορτίο στην επιφάνεια του στερεού και όταν αυτό βρίσκεται σε υγρό περιβάλλον με άλλα ιόντα τότε προκαλείται η ανάπτυξη μιας στιβάδας ιόντων η οποία στη συνέχεια αποκτά ένα επαγόμενο ηλεκτρικό φορτίο.

Αυτά τα ηλεκτρικά φορτία δίνουν με τη σειρά τους ένα δυναμικό σε κάθε στιβάδα, το οποίο εξαρτάται από την πυκνότητα του ηλεκτρικού φορτίου. Η συγκέντρωση τόσο των ιόντων όσο και το ηλεκτρικο φορτίο μεταβάλλονται ενώ προσεγγίζεται το υγρό περιβάλλον, δημιουργώντας βαθμίδα δυναμικού. Το ερώτημα που προκύπτει είναι σε ποιά θέση το δυναμικό έχει φυσική σημασία και χαρακτηρίζει την επιφάνεια και ουσιαστικά μπορεί να αποδοθεί στο υλικό. Η τιμή του δυναμικού στη θέση στην οποία μπορεί να μετρηθεί και ουσιαστικά να αποδοθεί στο υλικό ονομάζεται ζ-δυναμικό.

Στις διάφορες θεωρίες υπάρχει τμηματοποίηση των στιβάδων με διάφορα ονόματα και με διαφορετικά χαρακτηριστικά. Στην πραγματικότητα, αυτές οι στιβάδες δεν αποτελούν οριοθετημένες κανονικές στιβάδες αλλά είναι αποτέλεσμα μιας προσπάθειας κατηγοριοποίησης της συμπεριφοράς της διεπιφάνειας και διευκόλυνσης της μαθηματικής τους μοντελοποίησης.

Με αφετηρία αυτές τις διαπιστώσεις αναπτύχθηκαν οι εξισώσεις που περιγράφουν την διπλοστιβάδα προκειμένου να καταστεί δυνατή η μέτρηση του ζ-δυναμικού αλλά και να προσδιοριστούν τα μεγέθη από τα οποία εξαρτάται. Στα πειράματα μελετήθηκαν πλακίδια SiO_2 με τη βοήθεια του μηχανήματος Zeta-Cad παίρνοντας μετρήσεις σε περιβάλλοντα με διαφορετικά pH. Η μέτρηση του ζ-δυναμικού στα πειράματα στηρίχθηκε στη μέθοδο της δημιουργίας δυναμικού μέσω ροής (streaming potential).

Το ρεύμα μέσω ροής (streaming current) και το δυναμικό μέσω ροής εμφανίζονται γενικά λόγω της μετατόπισης φορτίου στην ηλεκτρική διπλή στιβάδα που προκαλείται από μια εξωτερική δύναμη μετατόπισης της υγρής φάσης εφαπτομενικά προς το στερεό.

Η μεταφορά των υδροδυναμικά κινητικών ιόντων στην διεύθυνση της ροής του υγρού μπορεί να ανιχνευθεί άμεσα. Αυτό γίνεται είτε με τη μέτρηση του ηλεκτρικού ρεύματος μεταξύ δύο θέσεων ανάντη και κατάντη της ροής, μέσω μη πολωμένων ηλεκτροδίων τα οποία έχουν επαρκώς χαμηλή εσωτερική αντίσταση ώστε να αγνοηθεί η ύπαρξη του αντίθετου ρεύματος (back current) μέσα σε κανάλι ροής.

Εναλλακτικά, το ηλεκτρικό δυναμικό μπορεί να μετρηθεί μεταξύ των δύο ηλεκτροδίων ανάντη και κατάντη της ροής, εάν η εσωτερική αντίσταση του χρησιμοποιούμενου ηλεκτρόμετρου είναι αρκετά υψηλή (μέτρηση δυναμικού λόγω ροής). Για τον προσδιορισμό του δυναμικού στην περιοχή της διπλοστιβάδας λόγω της κινητικότητας των ηλεκτρικών φορτίων διατυπώθηκαν σχέσεις οι οποίες ποσοτικοποιούν την ένταση του παρατηρούμενου ηλεκτροκινητικού φαινομένου.

Για τη διεξαγωγή των πειραμάτων αυτής της διπλωματικής εργασίας έγινε χρήση του προαναφερθέντος μηχανήματος Zeta-Cad. Είναι ένα μηχάνημα σχεδιασμένο για να μελετήσει τις ιδιότητες κολλοειδών και επιφανειακών φορτίων των σωματιδίων καθώς και επίπεδων επιφανειών. Η βασική αρχή λειτουργίας του εξηγείται στο κεφάλαιο που αφορά το δυναμικό μέσω ροής που προκύπτει όταν ένα υγρό ρέει μέσα σε ένα τριχοειδές κανάλι που δημιουργείται από δύο παράλληλες επιφάνειες.

Η μηχανή αναγκάζει το υγρό να ρέει λόγω διαφοράς πίεσης Δp και ταυτόχρονα μετρά το δυναμικό συνεχούς ροής κατά μήκος του καναλιού. Το δυναμικό συνεχούς ροής μετράται με την ύπαρξη δύο ηλεκτροδίων μόλις πριν την είσοδο και ένα αμέσως μετά την έξοδο του καναλιού. Το μηχάνημα αυτό προκειμένου να μετατρέψει τα δεδομένα πίεσης και ηλεκτρικού δυναμικού που λαμβάνει σε τιμές ζ-δυναμικού εφαρμόζει την απλοποιημένη σχέση του Helmholtz-Smulowksi [13] .

Η σχέση αυτή βασίζεται στις παραδοχές ότι:

- Η ροή είναι στρωτή και ανεπτυγμένη
- Το μέγεθος του τριχοειδούς καναλιού είναι μεγάλο σε σχέση με την διάμετρο της διπλής στιβάδας
- Μηδενική επιφανειακή αγωγιμότητα (η οποία συνήθως μπορεί να γίνει σημαντική όταν το ζ-δυναμικό είναι μεγάλο (π.χ., | ζ |> 50 mV).

Εγιναν μια σειρά από πειράματα τα οποία είχαν σκοπό την αναπαραγωγή προηγούμενων μετρήσεων προκειμένου να διαπιστωθεί η λειτουργικότητα του μηχανήματος καθώς και τον προσδιορισμό κάποιων τιμών αναφοράς. Τα πρώτα πειράματα έγιναν με πλάκες SiO_2 με ηλεκτρολύτη KCl και σε περιβάλλοντα με διαφορετικές τιμές pH. Ακολουθήθηκε το πρωτόκολλο του εργαστηρίου και έγιναν 3 μετρήσεις για κάθε σημείο.

Με τα πρώτα αποτελέσματα του πειράματος ήταν σαφές ότι η μέτρηση του ζ-δυναμικού των πλακιδίων SiO_2 είναι πιο περίπλοκη από ότι αναμενόταν. Μια σειρά από απροσδόκητες μετρήσεις οδήγησε στον σχεδιασμό περισσοτέρων πειραμάτων.

Συγκεκριμένα αποφασίστηκε να γίνουν περαιτέρω μετρήσεις σε πλάκες SiO_2 σε διαφορετικές συγκεντρώσεις KCl και μια ακόμα πιο λεπτομερής γραφική παράσταση (ζ-δυναμικού-pH), ιδίως στα σημεία καμπής. Το KCl επιλέχθηκε επειδή είναι ένας 1:1 σθένους ηλεκτρολύτης και για την εξίσωση των Helmholtz-Smulowksi είναι πιο ακριβής. Επίσης υπάρχουν πλούσια βιβλιογραφικά στοιχεία που αφορούν πειράματα με αυτό τον ηλεκτρολύτη και γι 'αυτό είναι πιο εύκολο να συγκριθούν τα αποτελέσματα και να εξαχθούν πιο ασφαλή συμπεράσματα.

Επιπλέον, με βάση τα ήδη ληφθέντα δεδομένα έγινε κατανοητό ότι η δομή της επιφάνειας του πλακιδίου παίζει σημαντικό ρόλο για τη μέτρηση και την αξιοποίηση του ζ- δυναμικού. Δεδομένου ότι το πυρίτιο είναι ένα υλικό που έχει μελετηθεί εκτενώς από προηγούμενους ερευνητές, αποφασίστηκε ότι ένα νέο

πρωτόκολλο ειδικά γι 'αυτό θα πρέπει να γίνει, όπως και ότι η μέτρηση του ζ-δυναμικού μπορεί να χρησιμεύσει ως σημείο αναφοράς για τις μελλοντικές μετρήσεις και μελέτες.

Για να επιτευχθεί αυτό, αποφασίστηκε μια ειδική διαδικασία για την επιφανειακή επεξεργασία που θα πρέπει να προηγείται των μετρήσεων. Η διαδικασία στοχεύει στην εξάλειψη του στρώματος οξειδίου που σχηματίζεται σε επαφή με τον αέρα λόγω της σύνδεσης του οξυγόνου με το πυρίτιο. Υστερα από την κατεργασία η επιφάνεια εχει αποδεσμευτεί από το δεσμευμένο οξυγόνο. Στη συνέχεια αφήνοντας τα δείγματα σε ατμοσφαιρικό περιβάλλον για ένα συγκεκριμένο χρονικό διάστημα αναπτύσεται εκ νέου ένα επιφανειακο στρώμα SiO_2 το πάχος του οποίου εξαρτάται από το χρονικό διάστημα που το πυρίτιο βρίσκεται σε επαφή με την ατμόσφαιρα. Σκοπός της κατεργασίας αυτής ήταν να επιτευχθεί ομοιογένεια και μείωση της τραχύτητας της επιφάνειας.

Για την καλύτερη κατανόηση αλλά και για την εξασφάλιση της αξιοπιστίας των παραπάνω μετρήσεων παρακολουθήθηκε η συμπεριφορά της ροής για να επιβεβαιωθεί η βασική υπόθεση ότι η ροή στο τριχοειδές που σχηματίζεται ανάμεσα στις δύο πλάκες είναι στρωτή και ανεπτυγμένη. Έτσι ο ρυθμός ροής μετρήθηκε στις πιέσεις 0-0.35 bar που εφαρμόστηκαν.

Οι μετρήσεις έγιναν με την αφαίρεση ενός από τα δοχεία του μηχανήματος και υπό σταθερή πίεση στην έξοδο του ηλεκτρολύτη που ρέει ανάμεσα στις πλάκες μετρήθηκε ο όγκος του για μια περίοδο 1 min. Στη συνέχεια χρησιμοποιήθηκαν οι εξισώσεις Navier-Stokes για τον υπολογισμό της ροής στο κανάλι που σχηματίζεται από τα δύο πλακίδια.

Μετά από επεξεργασία των αποτελεσμάτων και σε συνδυασμό με τη βιβλιογραφική ανασκόπιση συμπεραίνεται ότι διαφορετικοί ερευνητές βρίσκουν συχνά διαφορετικές τιμές ζ-δυναμικού για όμοια περιβάλλοντα. Μερικές φορές, οι επιφάνειες δεν είναι στην πραγματικότητα πανομοιότυπες: η υψηλή ειδική επιφάνεια και η επιφάνεια δραστικότητας των κολλοειδών συστημάτων καθιστούν την τιμή ζ-δυναμικού πολύ ευαίσθητη ακόμη και σε μικρές ποσότητες ακαθαρσιών στο διάλυμα. Αυτό μπορεί εν μέρει να εξηγήσει διακυμάνσεις για τους ηλεκτρο-κινητικούς προσδιορισμούς από το ένα εργαστήριο στο άλλο. Εναλλακτικά, δεδομένου ότι το ζ-δυναμικό δεν είναι μια άμεσα μετρήσιμη ποσότητα, είναι πιθανό οι διακυμάνσεις να οφείλονται στην επιλογή ενός ακατάλληλου μοντέλου για τη μετατροπή του ηλεκτρο-κινητικού σήματος σε ζ-δυναμικό. Το επίπεδο εξειδίκευσης που απαιτείται (για το μοντέλο) εξαρτάται από την κατάσταση και την επιθυμητή ακρίβεια στην μέτρηση. Η επιλογή της τεχνικής της μέτρησης και της θεωρίας που χρησιμοποιείται εξαρτάται σε μεγάλο βαθμό από το σκοπό της έρευνας των ηλεκτρο-κινητικών φαινομένων.

Υπάρχουν περιπτώσεις στις οποίες μπορεί να δικαιολογηθεί η χρήση απλών μοντέλων, ακόμη και αν δεν αποδίδουν το σωστό ζ-δυναμικό. Για παράδειγμα, εάν οι ηλεκτρο-κινητικές μετρήσεις χρησιμοποιούνται ως ένα είδος εργαλείου ελέγχου

ποιότητας, το ενδιαφέρον βρίσκεται στην ταχεία (on-line) ανίχνευση των εναλλαγών της ηλεκτρικής κατάστασης του περιβάλλοντος και όχι στην απόκτηση ακριβών τιμών του ζ-δυναμικού. Από την άλλη πλευρά, όταν ο σκοπός είναι να συγκριθούν υπολογισμένες τιμές του ζ-δυναμικού του συστήματος κάτω από δεδομένες συνθήκες, χρησιμοποιώντας διαφορετικές ηλεκτρο-κινητικές τεχνικές, μπορεί να είναι απαραίτητο να βρεθεί μια πραγματική τιμή του ζ-δυναμικού. Το ίδιο ισχύει και για εκείνες τις περιπτώσεις στις οποίες θα χρησιμοποιηθούν οι τιμές ζ-δυναμικού για την εκτέλεση υπολογισμών άλλων φυσικών ποσοτήτων όπως η ενέργεια Gibbs αλληλεπίδρασης μεταξύ των σωματιδίων.

Συμπερασματικά προκύπτει ότι η μελέτη του ζ-δυναμικού είναι μια πολύ σημαντική τεχνική χαρακτηρισμού των υλικών και μπορεί να δώσει χρήσιμες πληροφορίες για την συμπεριφορά των υλικών σε ρευστά περιβάλλοντα. Η αξιολόγηση του ζ-δυναμικού δημιουργεί προβλήματα, δεδομένου ότι, αν και είναι αρκετά εύκολο να ορισθεί ως τιμή (είναι γνωστό από τι εξαρτάται), εν τούτοις υπάρχουν μεγάλες αποκλίσεις για θεωρητικώς ταυτόσημες επιφάνειες μεταξύ των μελετών των διαφόρων έρευνητικών ομάδων. Αυτό οφείλεται στο ότι ακόμη και η μικρότερη μεταβολή στο περιβάλλον μπορεί να επηρεάσει την ισορροπία στη διπλοστιβάδα.

Όσον αφορά το Zeta-Cad, είναι κατάλληλο για τον προσδιορισμό του ισοηλεκτρικού σημείου των υλικών το οποίο φαίνεται να είναι η πιο χρήσιμη τιμή για τον χαρακτηρισμό της επιφάνειας, δεδομένου ότι είναι μοναδική για κάθε υλικό. Σχετικά με τη χρήση του ζ-δυναμικού σε πιο εξελιγμένα υλικά γίνεται εμφανής η σύνδεση της τιμής αυτής με την επιφάνεια του υλικού. Με σταθερές συνθήκες μπορεί να χρησιμοποιηθεί ως μέθοδος χαρακτηρισμού αλλά και εξακρίβωσης αλλαγών στην επιφάνεια.

Ορολογία:

- Double layer (Διπλοστιβάδα): Αποτελεί τη στιβάδα η οποία δημιουργείται στην επιφάνεια ενός στερεού όταν βρίσκεται σε υγρό περιβάλλον και απαρτίζεται από τα ιόντα που είναι διεσπαρμένα στο υγρό και έχουν προσδεθεί στην επιφάνεια λόγω ηλεκτροστατικών δυνάμεων σχηματίζοντας κατά βάση 2 διαφορετικά στρώματα το ένα δίπλα στο άλλο με αντίθετά φορτία.

- Streaming potential, U_{StR} (V), είναι η διαφορά δυναμικού όταν δεν υπάρχει ηλεκτρικό ρεύμα στο σύστημα, που προκαλείται από τη ροή του υγρού υπό βαθμίδα πίεσης μέσω ενός τριχοειδούς διαφράγματος ή μεμβράνης. Η διαφορά μετράται κατά μήκος του συστήματος που εμφανίζεται η διπλοστιβάδα ή ανάμεσα στα άκρα του τριχοειδούς. Το streaming potential δημιουργείται από τη συσσώρευση φορτίου που προκαλείται από τη ροή των αντίθετων φορτίων από αυτά των επιφανειών στο εσωτερικό των τριχοειδών αγγείων ή πόρων.

- Dielectric dispersion (Διηλεκτρική διασπορά) είναι η μεταβολή της διηλεκτρικής σταθεράς σε ένα αιώρημα κολλοειδών σωματιδίων με τη συχνότητα ενός εφαρμοσμένου εναλλασσόμενου ρεύματος (AC) πεδίου. Για χαμηλές και μεσαίες συχνότητες η αλλαγή αυτή συνδέεται με την πόλωση του ιοντικού φορτίου. Συχνά, μόνο η διηλεκτρική διασπορά χαμηλής συχνότητας (LFDD) διερευνάται.

Summary

In this diploma thesis, z-potential measurements on silicon planar substrates using a Zeta-CAD machine are investigated. In the first part, there is a brief presentation of the theoretical basis behind the z-potential and the related phenomena. This includes the theory of the double layer in colloidal systems the models and approaches of the silica-aqueous interface as well as the estimation of the equations of the total charge in the diffusive layer.

In the second part, the experiments of z-potential measurements on silicon substrates (with a passive silica native layer) are detailed with a special care on reproducibility of the measurements. These experiments were conducted in order to have a basis and a reference point for future experiments concerning more advanced materials.

In the conclusions the results are discussed, the potential uses of the Zeta-Cad machine are outlined in the framework of the laboratory's research interests and a new protocol was proposed. Special interest was given in the reproducibility of the results and the investigation of the factors that influence the trust upon the measurment of z-potential. The further experiemnts concerning the flow behavior, an essential part of the z-potential measurement with the streaming potential method, gave useful information on how to approach the measurement of z-potential and helped to establish the new protocol.

Introduction

The measurement of the z-potential of materials has been a significant technique since the early years of the 20th century although the exact mechanisms around the surface energy were still not fully understood. Nowadays the measurement of the z-potential is widely used in many industrial procedures and applications especially where colloidal systems are concerned.

In particular the measurement of the surface z-potential has a great range of applications regarding the control, stability or flocculation/coagulation, of colloidal systems. By measuring the z-potential the electric charge of the double layer is revealed, thus allowing for an excessive control on the systems behavior since the double layer is the primer electrochemical phenomenon existing in a solid-liquid system.This practically means that by knowing the electric charge of the materal we can control the stability of the system, either by changing the enviroental conditions or the factors that built the electri charge. This is clearer in the following exmaples of suspensions and dispertions of materials in different enviroments.

The applications of the z-potential are more common and evident in the following areas (Zeta-potential, a complete course, 2008, p.1)[2] :

-Minerals & Ores: The techniques for retrieving several minerals such as lead, zinc and copper include the suspension of their particles in water. Flotation is next needed for the recovery of the mineral. The efficiency of the procedure can be control through the z-potential of the particles. Also z-potential has been used to control the viscosity of coal slurries reducing their potential environmental threat.

-Clays & Drilling Fluids: Dispersions of clays in water or other fluids are really common in paper plastic and synthetics industry. Therefore the tailoring of their characteristics through the control of the dispersions helps in achieving the desired properties for each task.

-Ceramics: slip casting is used in volume production of ceramic ware. Suspensions are common in these technic. The structure of the clay layer depends on the degree of dispersion of the clay suspension. Affecting the pH affects the apparent viscosity of clays and z-potential is the tool to achieve that.

-Paints: The pigments in paint must be well dispersed in order for the paint to perform successfully. Z-potential measurements can be used in this application to control the composition of the paint and the amount of additives required for an optimum dispersion.

-Water and Wastewater Coagulation: Waste water and water comes always with dispersed particles. Therefore in the treatment procedures where the colloidal solids are the

most difficult to remove because of their size the key for an effective removal is the reduction of their z-potential so flocculation takes place, enabling the rapid and easy removal of these particles.

Whereas Zeta potential measurements were first developed for suspensions (as detailed before), this thesis focuses on zeta potential of planar substrates. Indeed, the characterization of the surface potential (or z-potential) of a material is an important issue to investigate the interactions between the material and its immersion medium (for example adhesion of micro-organisms, salts on immersed samples). This surface potential can also be helpful to characterize the surface of a sample and its evolution, even if the sample does not operate in a liquid medium. Here is the general context and the final objective of the thesis: to use the z-potential measurements to follow the evolution of a piezoelectric material before and after immersion in plasma discharge. As plasma deals with charged particles, z-potential measurement (even in liquid) could be relevant to understand the interaction between the piezoelectric material and the plasma discharge.

In the 1st chapter there is a presentation of the mayor electrokinetic phenomena that develop on a material surface while in different enviroments. The structure of the double layer is investigated through the theories that have been introduced during the past years. For the better understanding of the z-potential the equations that describe the electric charge on the diffuse layer are developed. Last chapters are used to explaine the conditions and the experiments organized during this thesis. Finally the results are discussed in order to conduct useful conclusions about the importance of the z-potential measurement.

Chapter 1: Theoretical part

1.1 Introduction

The z-potential (ζ) value is a significant tool regarding the understanding and the measurement of surface energy and behavior of solid liquid systems. The heart of the phenomena is the interface of the two phases, where there is a dispersion of ions and other particles near the solid liquid boundaries.

The first step on understanding the meaning of z-potential is explaining the phenomenon of double layer that is created on surfaces of solids when in a liquid. Therefore it is important to explain and understand the mechanisms around this double layer which is responsible for the behavior of most of the solids in liquid environments.

The development and the explanation of the phenomena in this particular region, that exceeds no more than some nm in dimensions, is what most studies and theories have focused on. The two main parameters are the extent of the interfacial chemistry and the interface itself. These two parameters are the ones that influence and control the nature and behavior of all two phased systems.

In terms of information contained in the measurement of the z-potential it is shown that the value is related to the surface charge. This is a property all material possesses when in a fluid. In practice the value and the sign of z-potential affect the procedure, the way of treatment and many products specifications and controls. The simplest information z-potential can give is the charge of the surface studied and in further analysis can provide information about the electro kinetic phenomena occurring at the interface of the partical and its environment.Moreover it can help to improve product quality and performance in a commercial/industrial level.

All materials will spontaneously acquire a surface electrical charge when brought into contact with a polar medium (i.e., water). Generally an interface in deionized water is negatively charged, but there are materials that can be positively charged. The various charging mechanisms according to Particle sciences (2008)[1] are:

1. Electron affinity differences of two phases
2. Ionization of surface groups
3. Differential ion adsorption from electrolyte solution
4. Differential ion dissolution from a crystal lattice
5. Surface anisotropy
6. Isomorphous substitution

In this thesis where silicon/water interface is studied the second mechanism,the one that causes the development of a double layer, is the most interesting. Most of the models attempting to describe the interface take into consideration the surface electric charge and the charges of the particles inside the medium in order to predict the thickness of the double layer.

In general this mechanism is observed with all metal oxide surfaces (M-OH) as well as materials that contain carboxyl and/or amino groups. This latter category includes proteins, ionic polymers, and polyelectrolytes, many of which are widely utilized in pharmaceutical formulations. The ionization and/or dissociation of these groups (degree of charge development) and the net molecular charge (and thus sign, either positive or negative) depends strongly on the pH of the dispersion media.

1.2 Double layer

The double layer (from now on denoted as DL) refers to two parallels layers of electrically charged particles formed on a charged surface of a material when inside a fluid. Due to the electrostatic forces between the ions the opposite charges create a first layer. The creation of this layer has now created a ''surface'' of opposite charge (to the one of the actuel surface of the materal) and now absorbs counter ions creating a second layer with an opposite charge.This eventually leads at a double layer of absorbed ions on the material.

The material might be a solid particle, a gas bubble, a liquid droplet, or a porous body.

1.2.1 Theories and models developed

Helmhotz approach

Although many models for the double layer have been published in the literature, there is no general model that can be used in all experimental situations. This is because the double-layer structure and its capacity depend on several parameters such as: material (metals, carbons, semiconductors, electrode porosity, the presence of layers of either oxides or polymeric films or other solid materials at the surface), type of solvent, type of supporting electrolyte, extent of specific adsorption of ions and molecules, and temperature.

The existence of the double layer was first proposed by Helmholtz as described in Lyklema, J.(1991)[13] , tried to explain the phenomena accuring when an electrode was present in an electrolyte. Helmholtz was the first to realize that at the ''electrolyte-electrode'' system a boundary between the surface of the material and the rest of the bulk liquid is formed, creating an interfacial area where ions and other particles are absorbed and diffused therefore having an alternation in the concentration of ions (in comparison to the rest of the liquid) around the surface of the material.

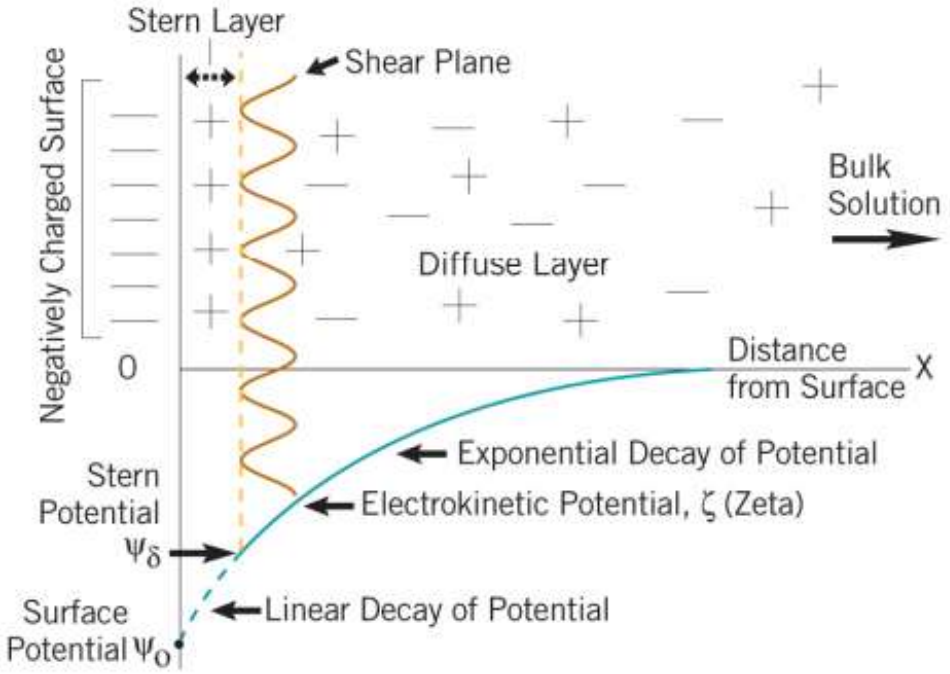

Figure 1. Simplified model of the electric double layer [1]

Beginning from the surface of the material the distribution of the electrical charges at the interface differs from that in the bulk liquid phase. As shown in fig,1 a “structure”, called the electric double-layer (EDL) develops in such a way that the particle surface charge is neutralized by an adjacent layer in solution containing an excess of ions of opposite charge to that of the surface, i.e., counter ions; ions of the same charge as the surface are termed coins. The two layers are compromised by one layer called the Stern layer which is the closest to the surface and contains absorbed ions considered immobile and a second one called the diffused layer from which ions can be distributed randomly according to the influence of electrical forces and thermal motion.

Each particle is surrounded by oppositely charged ions in the Stern layer. Beyond the stern layer there are both positive and negative ions in what can be considered a charge “cloud”. These along with the ions in the stern layer form the electrical double layer at the particle-liquid interface. The ions within the charge cloud or “diffuse” region move freely and while moving away from the surface the potential dromps exponentially ntil eventuelly decays to zero. The potential at the boundary of the Stern plane and the diffuse (shear) plane is known as the z- potential. Therefore the shear plane is the part of the diffuse layer where the value of the z-potential is measured.

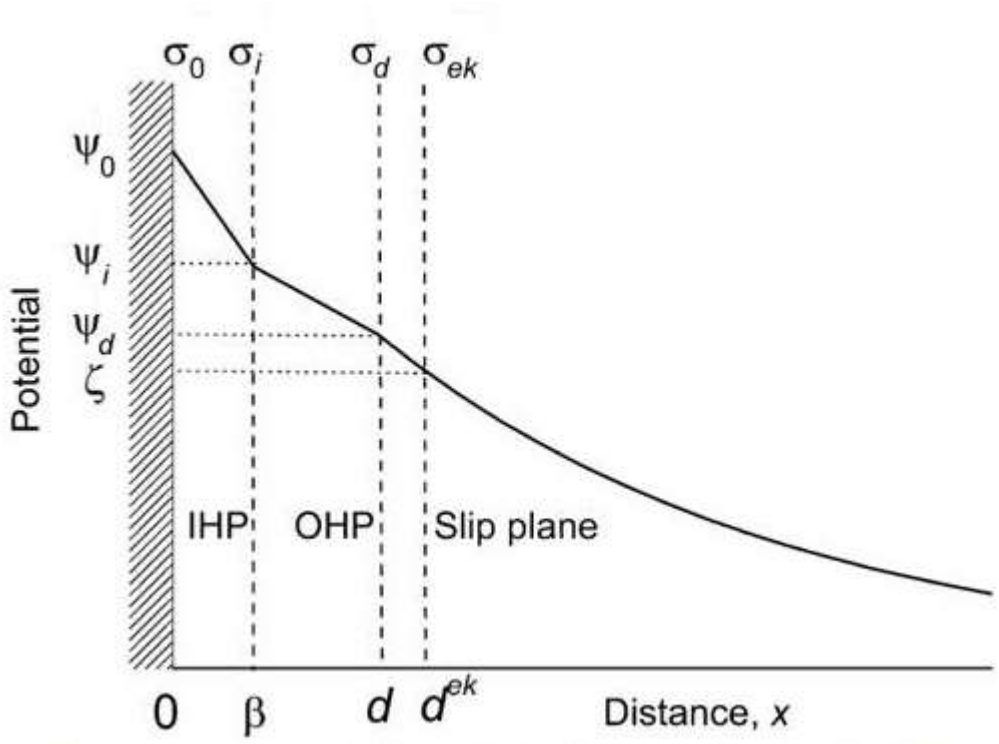

Figure 2. Schematic representation of the charges and potentials at a positively charged interface. The region between the surface (electric potential ψ0; charge density 0) and the IHP (distance β from the surface) is free of charge. The IHP (electric potential ψ_i; charge density σ_i) is the locus of specifically adsorbed ions. The diffuse layer starts at x = d (OHP), with potential ψ_d and charge density σ_d. The slip plane or shear plane is located at x = d^{ek}. The potential at the slip plane is the electrokinetic or z-potential, z; the electrokinetic charge density is σ_{ek} [1]

The Stern layer is then subdivided into an *inner Helmholtz layer* (IHL), bounded by the surface, the *inner Helmholtz plane* (IHP) and an *outer Helmholtz layer* (OHL), located between the IHP and the *outer Helmholtz plane* (OHP). This situation is shown in Fig. 2 for a simple case. The necessity of this subdivision may occur when some ion types (possessing a chemical affinity for the surface in addition to purely Coulombic interactions), are specifically adsorbed on the surface, whereas other ion types interact with the surface charge only through electrostatic forces. The IHP is the locus of the former ions, and the OHP determines the beginning of the diffuse layer, which is the generic part of the electric double layer (EDL) (i.e., the part governed by purely electrostatic forces). The fixed surface-charge density is denoted σ_0, the charge density at the IHP σ_i , and that in the diffuse layer σ_d. And since the system is electroneutral :

$$\sigma_0 + \sigma i + \sigma_d = 0 \qquad [1]$$

As isolated particles cannot be linked directly to an external circuit, it is not possible to change their *surface potential* at will by applying an external field. Contrary to mercury and other electrodes, the surface potential, ψ_o , of a solid is therefore not capable of

operational definition, meaning that it cannot be ambiguously measured without making model assumptions.

As a consequence, for disperse systems it is the surface charge that is the primary parameter, rather than the surface potential. The potential at the OHP, at distance *d* from the surface, is called the *diffuse-layer potential*,ψ_d (sometimes also known as *Stern potential*): it is the potential at the beginning of the diffuse part of the double layer.
The potential at the IHP, located at distance β ($0 \leq \beta \leq d$) from the surface, the *IHP potential*, is given the symbol ψ_i . All potentials are defined with respect to the potential in bulk solution.

The electric potential decreases linearly from ψ_0 (the actual thermodynamic surface potential) to the Stern potential, ψ_d and then it decays exponentially to zero in the diffuse layer. This is described by:

$$\psi = \psi_d \exp [- \kappa x] \qquad [2]$$

where, x is the distance from the material surface and κ, called the Debye-Hückel parameter or Debye lenght, is defined as:

$$\kappa = [2e^2 NAcz^2 / \varepsilon\varepsilon_0 kbT]^{½} \qquad [3]$$

where, e is the protonic charge, NA is Avogadro's constant, c is the concentration of electrolyte of valence z, ε is the dielectric constant, ε_0 is the permittivity of free space and k_b is the Boltzmann constant.

Hence, it can be seen that the electric potential depends (through κ) on the ionic composition of the medium. If κ is increased (the electric double layer is "compressed") then the potential must decrease.

The Gouy-Chapman model

According to this model the capacitance is not a constant and it depends on the applied potential and the ionic concentration. The "Gouy-Chapman model" as seen in Brian J. Kirby et al. (2004)[6] made significant improvements by introducing a diffuse model of the DL. In this model the charge distribution of ions as a function of distance from the metal surface allows Maxwell–Boltzmann statistics to be applied. Thus the electric potential decreases exponentially away from the surface of the fluid bulk

The *diffusive layer* is also known as Gouy-Chapman layer or electric double layer. Here, it is shown the one-dimensional formulation of the equation for a $1:1$ electrolyte:

$$\frac{\mathrm{d}^2\Psi}{\mathrm{dx}^2} = -\frac{1000\, q\, n_A}{\varepsilon\varepsilon_o}([e^+] - [e^-]) \qquad [4]$$

ψ denotes the electrostatic potential, q the elementary charge, N_a Avrogado's constant, and e^{-+} the charge distributions for the positive and negative ions, in mol/L respectively. Assuming positive and negative ions in thermodynamical equilibrium with their

neighborhood, their ionic densities can be related to the electrostatic potential by the following Boltzmann distributions:

$$[e^+] = C_o\, e^{-\frac{q\,\psi}{K_B T}}$$

$$[e^-] = C_o\, \mathrm{e}^{\frac{q\,\psi}{K_B T}} \qquad [5]$$

Joining (5) and (4) leads to the Poisson-Boltzmann equation for a $1:1$ electrolyte:

$$\frac{\mathrm{d}^2\Psi}{\mathrm{dx}^2} = -\frac{q\,C_o}{\varepsilon\varepsilon_o}(e^{-\frac{q\,\psi}{K_B T}} - \mathrm{e}^{\frac{q\,\psi}{K_B T}})$$

$$\frac{\mathrm{d}^2\Psi}{\mathrm{dx}^2} = -\frac{2\,q\,C_o}{\varepsilon\varepsilon_o}\sinh(\frac{q\,\psi}{K_B T}) \qquad [6]$$

This ordinary non linear second order differential equation can only be solved analytically for very few cases and has to be treated with numerical methods.

The total charge density in the Gouy-Chapman layer can be calculated by (see appendix A):

$$\sigma_o = \pm\sqrt{8\varepsilon\varepsilon_o K_B T c_o}\,\sinh(\frac{q\,\psi}{K_B T}) \qquad [7]$$

Stern Modification

The Gouy-Chapman theory provides a better approximation of reality than does the Helmholtz theory, but it still has limited quantitative application. It assumes that ions behave as point charges, which they cannot, and it assumes that there is no physical limits for the ions in their approach to the surface, which is not true as it can be seen in figure 3. Stern[14] , therefore, modified the Gouy-Chapman diffuse double layer. His theory states that ions do have finite size, so cannot approach the surface closer than a few nm.

The first ions of the Gouy-Chapman Diffuse Double Layer are not at the surface, but at some distance d away from the surface. This distance will usually be taken as the radius of the ion. As a result, the potential and concentration of the diffuse part of the layer is low enough to justify treating the ions as point charges.

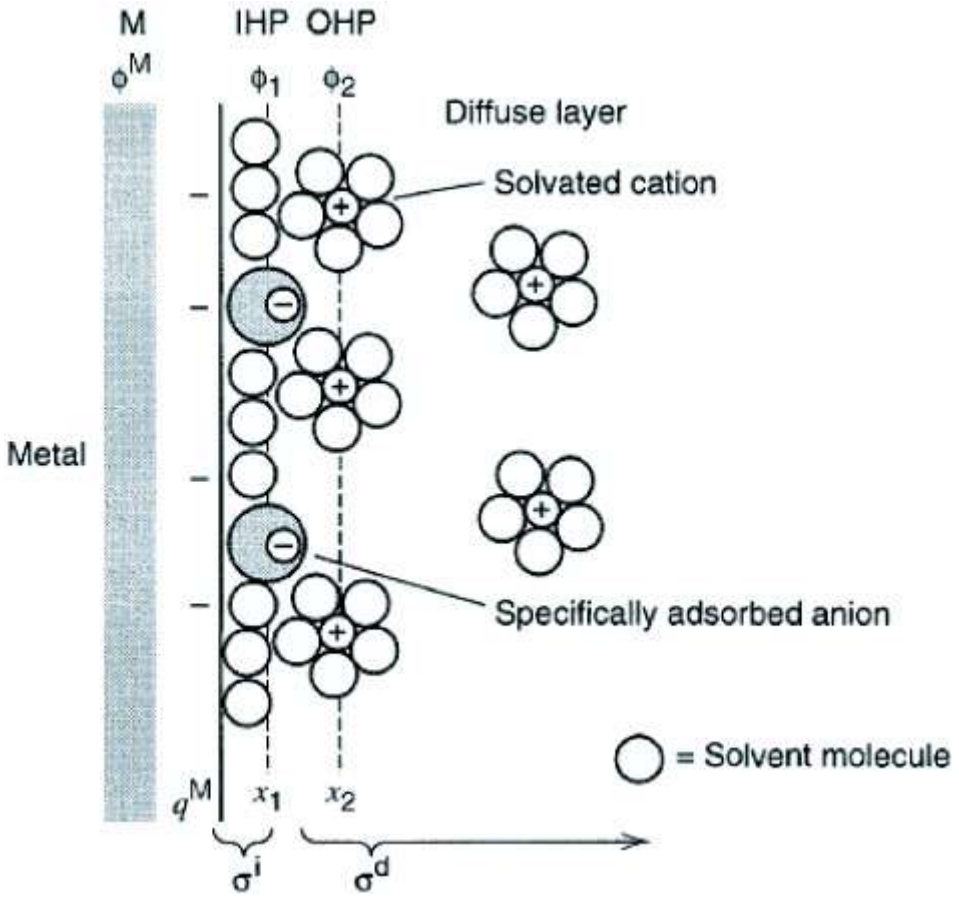

Figure 3. The different surface effects. The (non-) specific adsorbtion, due to (partial) release of the solvation shell and conjoint closer approach to the interface, the so called IHP, is depicted with white circles. The effect of surface complexation, due to the high affinity of attracting counter ions, is shown by the blue circles. The Stern layer ends at the OHP, the zone without counter ions exhibiting their full water shell (depicted with positively charged circles, surrounded by small surface circles), and is continued by the Gouy-Chapman layer [13].

Stern also assumed that it is possible that some of the ions are specifically adsorbed by the surface in the plane created by the absorbed ions, and this layer has become known as the Stern Layer. Therefore, the potential will drop by $\psi_o - \psi_d$ over the "molecular condenser" (ie. the Helmholtz Plane) and by ψ_d over the diffuse layer. ψ_d has become known as the z-potential. However, additionally to the Gouy-Chapmann and Stern contributions to the potential profile, several other effects exist. In general this effects are small and can be ignored. Some of these effects as can also be seen in the figure 3 are :

- *Specific Adsorbtion of Ions on the Surface.* This is caused by (partially) freeing the ions from their solvation shell and thus allowing them to be closer to the interface than the OHP. This new radius of closest approach is called Inner Helmholtz Plane (IHP). The total model, handling IHP and OHP, is called Gouy-Chapman-Stern-Graham model.

- *Non-Specific Adsorbtion.* Here, the ions keep their solvation shell, but are adsorbed onto the surface due to distant coulombic attraction.

- *Polarization of Solvent.* In general, the effects of electric field weakening due to the dipole movement of the water molecules is handled by adjusting the relative permittivity. This works well for the bulk, but in the vicinity of the surface many water molecules are not able to adjust to the electric field. So the relative permittivity will not be the same as for the bulk and can cause differences in the results (e.g. potential and charge distribution). However, at high electric fields, the description of the dielectric constant can become more complicate, due to dielectric saturation.

- *Surface Complexation.* Many charged surfaces exhibit an increased attraction to counter ions and enable the formation of complex compounds at the surface, changing the potential in their neighborhood.

The double layer is formed in order to neutralize the charged surface and, in turn, causes an electro kinetic potential between the surface and any point in the mass of the suspending liquid. This voltage difference is on the order of millivolts and is referred to as the surface potential. The magnitude of the surface potential is related to the surface charge and the thickness of the double layer.

While leaving the surface, the potential drops off roughly linearly in the Stern layer and then exponentially through the diffuse layer, approaching zero at the imaginary boundary of the double layer. The potential curve is useful because it indicates the strength of the electrical force between particles and the distance at which this force comes into play. A charged particle will move with a fixed velocity in a voltage field. This phenomenon is called electrophoresis.

The particle's mobility is related to the dielectric constant and viscosity of the suspending liquid and to the electrical potential at the boundary between the moving particle and the liquid. This boundary is called the slip plane and is usually defined as the point where the Stern layer and the diffuse layer meet. The relationship between z-potential and surface potential depends on the amount of ions in the solution.

1.3 Electro kinetic phenomena and streaming potential on liquid/solid interfaces.

1.3.1 Measuring techniques of z-potential

In this part the most important technique used fot the measurement of zeta potential will be presented along with the ir principles.

As z-potential is not directly measured the influence of this value upon the behavior of the meterials in diferrent conditions and eviroments are taken into consideration nd along with the right mathematical modelisation the signal obtained through the influence of z- potential upon different values of properties are used to be turned into z-potential values.

An important consequence of the existence of electrical charges on the surface of particles is that they interact with an applied electric field. These effects are collectively defined as electrokinetic effects. There are four distinct effects depending on the way in which the motion is induced. These are:

- **Electrophoresis:** the movement of a charged particle relative to the liquid it is suspended in under the influence of an applied electric field Electroosmosis: the movement of a liquid relative to a stationary charged surface under the influence of an electric field.

- **Electroosmosis:** the movement of a liquid relative to a stationary charged surface under the influence of an electric field.

- **Streaming potential:** the electric field generated when a liquid is forced to flow past a stationary charged surface Sedimentation potential: the electric field generated when charged particles sediment.

- **Sedimentation potential** - Creation of an electric field when a charged particle moves relative to stationary fluid.

A table has been created in order to sum up these techniques and compare them:

Technique	What is measured	What moves	What causes movement
Electrophoresis	Velocity	Particles move	Applied electric field
Electroosmosis	Velocity	Liquid moves in capillary	Applied electric field
Streaming potential	Potential	Liquid moves	Pressure gradient
Sedimentation potential	Potential	Particles move	Gravity=gΔρ

Table 1. Measurement techniques of z-potential.

The phenomena of streaming current and streaming potential occur in capillaries and plugs and are caused by the charge displacement in the EDL as a result of an applied pressure inducing the liquid phase to move tangentially to the solid. The *streaming current* can be detected directly by measuring the electric current between two positions, one upstream and the other downstream. This can be carried out via nonpolarizable electrodes, connected to an electrometer of sufficiently low internal resistance.

Streaming potential/current according to the Technical report of UIPAC[17] about the z-potentialmeasurements can be applied to study macroscopic interfaces of materials of different shape. Single capillaries made of flat sample surfaces (rectangular capillaries) and cylindrical capillaries can be used to produce micro-channels for streaming potential/current measurements.

Further, parallel capillaries and irregular capillary systems such as fiber bundles, membranes, and particle plugs can also be studied. Recall, however, the precautions already mentioned in connection with the interpretation of results in the case of plugs of particles. Other effects, including temperature gradients, potentials, or membrane potential can contribute to the observed streaming potential or electro-osmotic flow. An additional condition is the constancy of the capillary geometry during the course of the experiment. Reversibility of the signal upon variations in the sign and magnitude of Δp is a criterion for such constancy. Most of the materials studied so far by streaming potential/current measurements, including synthetic polymers and inorganic non-metals, are insulating. Either bulk materials or thin films on top of carriers can be characterized. Streaming potential/current measurements on samples of different geometries (flat plates, particle plugs, fiber bundles, cylindrical capillaries) each require their own set-up.

In this thesis for the measurement of the z-potential the streaming potential method was used. Therefore its principles are explained in detail.

1.3.2 Streaming potential

Streaming potential (difference), U_{str} (V), is the potential difference at zero electric current, caused by the flow of liquid under a pressure gradient through a channel, plug, diaphragm, or membrane. The difference is measured across the plug or between the ends of the channel. Streaming potentials are created by charge accumulation caused by the flow of counter-charges inside capillaries or pores

The quantities of the of streaming current and streaming potential occur in general due to the charge displacement in the electrical double layer caused by an external force shifting the liquid phase tangentially against the solid. This can occur when forming a slit channel between two parallel solid plates, and forcing the fluid to run through this channel and generate these quantites.

The convective transport of hydrodynamicaly mobile ions in the direction of the liquid flow can be either detected directly by measuring the electrical current between two positions up- and downstream via nonpolarizable electrodes by an electrometer of sufficiently low internal resistance to justify the neglection of the back current through the streaming channel (streaming current measurement).

Alternatively, the electrical potential can be measured between the two electrodes up- and downstream in the liquid flow if the internal resistance of the used electrometer is sufficiently high (streaming potential measurement). The measured streaming potential results from a steady state of the charge separation due to the streaming current and the back current in the streaming channel due to the specific electrical conductivity of the volume embedded. To determine the electrokinetic z-potential of the hydrodynamic phase boundary from streaming potentials or streaming currents, relations were established that involve a quantitative expression of the force that creates the observed electrokinetic phenomenon.

For that aim the liquid flow in the slit channel is determined only by the pressure difference across the channel assuming the fluid flow to be of the Hagen–poiseuille type. Since in the cases considered here the aspect ratio h/b of the cross section of the rectangular channel will not exceed 1/100, the channel can be assumed to consist of two parallel surfaces. The velocity profile of the liquid between two parallel plates for this case is parabolic and the wall shear rate is given according to:

$$\gamma=\left(\frac{dv}{dx}\right)_{x=(h/2)}=\frac{\left(\frac{h}{2}\right)\Delta p}{\eta L} \qquad [8]$$

Where γ is the wall shear rate, v the liquid velocity, x the distance from the center axis of the channel to a plane in the liquid parallel to the solid surfaces, h the distance between the parallel flat solid surfaces, η the dynamic viscosity of the fluid, and Δp the

pressure drop across the distance *L* that describes the lenght of the channel in the direction of the liquid flow .

Since the excess charge creating the net charge convection in the fluid flow is located in a thin layer close to the solid surface (as compared to the total distance of the flat sample surfaces), the wall shear rate given above can be used to give the velocity *V* of the liquid at any distance *y* from the wall relevant in terms of the thickness of the diffuse layer (the Debye radius):

$$V=\int_0^y \left(\frac{dv}{dx}\right)_{x=(h/2)} \quad , dy=\frac{\left(\frac{h}{2}\right)\Delta p\, y}{\eta L} \qquad [9]$$

Streaming current, Istr (A), is the current through the plug when the two electrodes are relaxed and short-circuited. The streaming current density, I_{str} (A/m^2), is the streaming current per area.The electrical charge entering with the liquid flow to create streaming current is given according to:

$$I_{str}=2b\int_{y=0}^{y=\frac{h}{2}} \rho(y)V(y)dy \qquad [10]$$

With ρ(y) being the volume charge density of the solution. At the channel that can be assumed to be formed of two parallel flat surfaces the one-dimensional variant of the poisson equation can be applied to express ρ(y) as:

$$\rho(y) = -\varepsilon\varepsilon_o \frac{d^2\Psi}{dy^2} \qquad [11]$$

where $\varepsilon\varepsilon_0$ is the dielectricity of the liquid solution and Ψ is the electrical potential at any position y.

Combining the eq [8-10] the streaming current

$$I_{str}=-\frac{\Delta p\varepsilon\varepsilon_o hb}{\eta L}\int_{y=0}^{y=h/2} y\frac{d^2\Psi}{dy^2}dy \qquad [12]$$

Following integration by parts:

$$I_{str}=-\frac{\Delta p \varepsilon \varepsilon_o h b}{\eta L}\left\{\left[y\frac{d\Psi}{\mathrm{dy}}\right]_{y=0}^{y=\frac{h}{2}} - [\Psi]_{y=0}^{y=h/2}\right\} \quad [13]$$

At y=0 ,Ψ becomes zero and designate ψ at y=h/2 becomes the electrokinetic potential ζ. So the last equation transforms to :

$$I_{str}=-\frac{\Delta p \varepsilon \varepsilon_o h b \zeta}{\eta L} \quad [14]$$

And by solving for ζ:

$$\zeta=-\frac{\eta\, I\, L}{\eta\, \Delta p\, \varepsilon\varepsilon_o\, h\, b\, L} \quad [15]$$

That is the main equation used in order to measure the z- potential via the measurement of the streaming current. Based on this equation and by applying that the streaming current does not run in a circuit a streaming potential U_{str} arises across the channel due to charge transport. The steady state created is developed but the balance of the streaming current and the back current caused by the bulk conductivity (K_β) and surface conductivity in the channel. Therefore:

$$I_{back}=\frac{hbUK_b}{L}+\frac{2bUK^\sigma}{L} \quad [16]$$

And by applying the steady state condition $I_{str}+I_{back}=0$:

$$\frac{\Delta p \varepsilon\, \varepsilon_o h b \zeta}{\eta L} = \frac{hbUK_b}{L} + \frac{2bUK^{\sigma}}{L} \qquad [17]$$

And by solving for ζ :

$$\zeta = \frac{\eta\, U_{str}}{\varepsilon\varepsilon 0\, \Delta p}\left(K_b + \frac{2K^{\sigma}}{h}\right) \qquad [18]$$

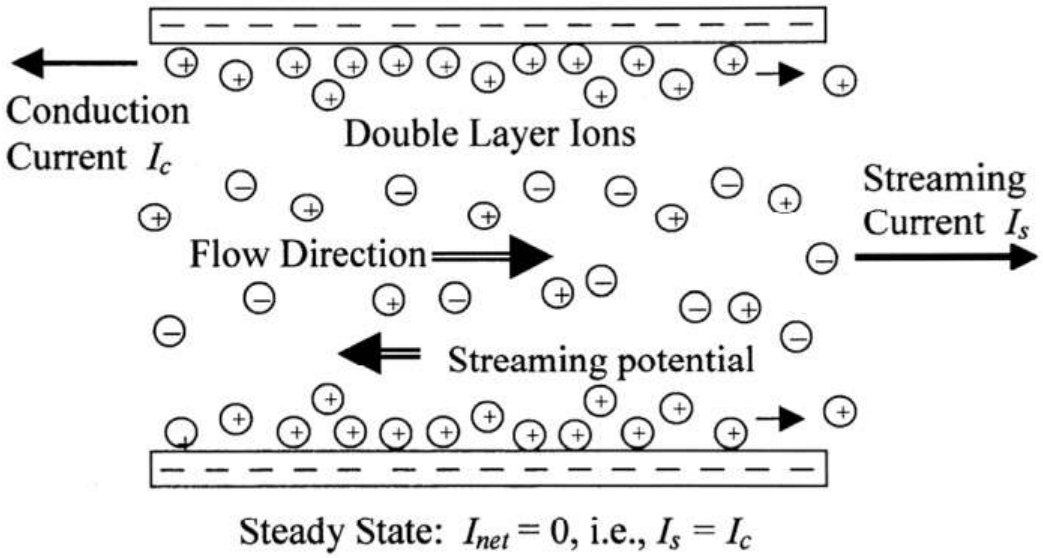

Figure 4. A snapshot of the channel created by two parallel plates while the liquid is in motion, along with the electrokinetic phenomena [18]

It can be observed from the above equations that the streaming current depends on the streaming channel dimensions for a given solution and pressure difference. The streaming potential in this case is a function of the total specific electrical conductivity of the channel. Equation [18] is frequently used in a simplified form neglecting 2*K*s/*h*, which is justified for large values of *h*.

This is our case where the main formula used is the following called the Helmholtz Smoluchowski[14] equation (HS):

$$\zeta = \frac{\eta\, U_{str}}{\varepsilon\varepsilon_o\, \Delta p} \qquad [19]$$

It is important to state that this equation assumes the following:

- the double layer is not too large compared to the pores or capillaries (i.e., $\kappa a \gg 1$), where κ is the reciprocal of the Debye length and the radius or the heigh of the channel
- there is no surface conduction (which typically may become important when the z- potential is large, e.g., |ζ| > 50 mV)
- there is no electrical double layer polarization
- the surface is homogeneous in properties
- there is not axial concentration gradient
- the geometry is that of a channel/tube.

Surface conductivity and electro kinetic phenomena

Continuing from the last part of the previous chapter it will further be investigated the role and the importance of the surface conductivity in the measurements of z-potential and the modeling of channels where streaming current and streaming potential arises. Recent studies have showed that along with electrokinetic measurements and titrations, the measurement of the surface conductivity (K^{σ}) is quite useful and can help to better characterize and understand the electrochemical behavior of solid surfaces [17].

Surface conduction is the excess electrical conduction tangential to a charged surface. It will be represented by the *surface conductivity*, *Kσ* (S), and its magnitude with respect to the bulk conductivity is frequently accounted for by the *Dukhin number*, *Du* .

The surface conductivity is the excessive charge quantity arising in addition to the bulk conductivity in solid liquid interfaces due to the charge accumulated in the electrical double layer. The study of the surface conductivity is also of interest regarding the assumptions made for the application of the eq [19]. So it is really helpful to understand how the surface conductivity works and becomes important for the measurement of z- potential, as it can improve our knowledge of when it should be taken into consideration or not. Following the previous equations development by combining eqquations [19] and [14] :

$$I_{str}=(K_b h+2K^{\sigma})\, U_{str}\, b/L \qquad [20]$$

And by solving for K^{σ} :

$$K^{\sigma}=1/2\left(\frac{I_{str}\, L}{U_{str}\, b}-K_B h\right) \qquad [21]$$

So by using this equation the conductivity of the surface can be determined given that the geometry of the channel is known as well as streaming current and potential data. This can

be achieved by taking into consideration that the ratio of streaming potential and streaming current results in the electrical resistance *R,* (or its inverse the conductance *C*) of the channel according to Ohm's law:

$$\frac{I_{str}}{U_{str}}=R_{channel}=\frac{1}{Ccap} \quad [22]$$

If the width and the length of the channel are fixed and the height of the channel (i.e., the distance between the parallel flat sample surfaces) is variable the condition for the channel height to be fulfilled in order to assume that surface conductivity can be neglected, for the proper evaluation of *K*s is given by:

$$Du=\frac{2K^{\sigma}}{K^{b}h}\geq 1 \quad [23]$$

Eq 23 expresses actually the condition regarding the surface conductivity under which the H-S equation can be used. It is really useful to have this numerical approach as it can be used in order to investigate (through the measurement of the surface conductivity) if the equation of HS is applicable and thus provide further trust to the z-potential results.

The importance of the surface conductivity can be further discussed and developed by applying the double layer theory on the equations above in order to obtain better ''view'' of its influence but such investigation exceeds the peruse of this report.

1.4 Isoelectric point

All charged materials will have what is termed an iso-electric point (IEP), defined as the condition when the value of ζ is zero. This is usually achieved by addition of *potential determining ions* (PDI) which, for many materials, means H+/OH- (i.e. a function of pH). It can also be attained by *specific adsorption* of charge modifying agents (CMA).

A plot of z-potential vs pH can be very useful since a number of important points can be noted from such data. The first is that, at the IEP, a particle suspension will have no resistance to aggregation as there is no longer any electrostatic repulsion between the particles. This is utilized in applications such as waste water treatment, where polyvalent ionic coagulants (such as alum) are used to remove unwanted suspended material – in particular colloidal sized particles – by aggregation followed by sedimentation/filtration. The optimum concentration is the one that reduces the ζ value to near zero ; addition of excess coagulant will result in re-stabilization that can be seen as a change in sign of ζ from positive to negative (or *vice versa*). Attempting to disperse materials in an IEP solution condition is futile. If the IEP is known then the sign of ζ can be determined from the solution pH.

The second point is that the magnitude of ζ increases (either side of the IEP) but eventually plateaus. Typically, this is the condition of maximum dissociation of any surface functional groups and this feature can be used to great effect when dispersing particles; the greater the magnitude of ζ the less the need for any additional dispersing aid. For proteins and charged macromolecules the ζ value at this plateau generally increases (becomes more positive or more negative) with increasing MWt; for example, at pH 9 the ζ of different grades of gelatin can range from as low as -15mV to more than -50mV [4]. It should also be apparent that materials that carry a negative charge can be made to be positive by simple addition of PDI or CMA. This can be used to affect both particle-particle and particle-substrate interactions both of which impact formulation and use of suspensions.

Thirdly, particles with an IEP <pH7 have an acidic character while those with an IEP >pH 7 are basic. A striking example of this is carbon black. The surface chemical properties are determined to a large extent by the distribution of oxygen-, hydrogen-, nitrogen- and sulfur-containing functional groups. The acid-base characteristics can be varied during manufacture and various after-treatments. Acidic carbon blacks typically have an IEP in the pH range 3-4, while basic blacks have an IEP in the pH range 8-9.

This also has implications for the process of dispersing materials not only in the choice of an ionic dispersant (anionic or cationic) but also in the choice of suspending medium (especially non-aqueous media and mixed solvents). However, all the values should be viewed as guides only and must be used with reservation - the actual value for a particular material can be influenced by its source or preparation method, pre-treatment and presence of trace impurities

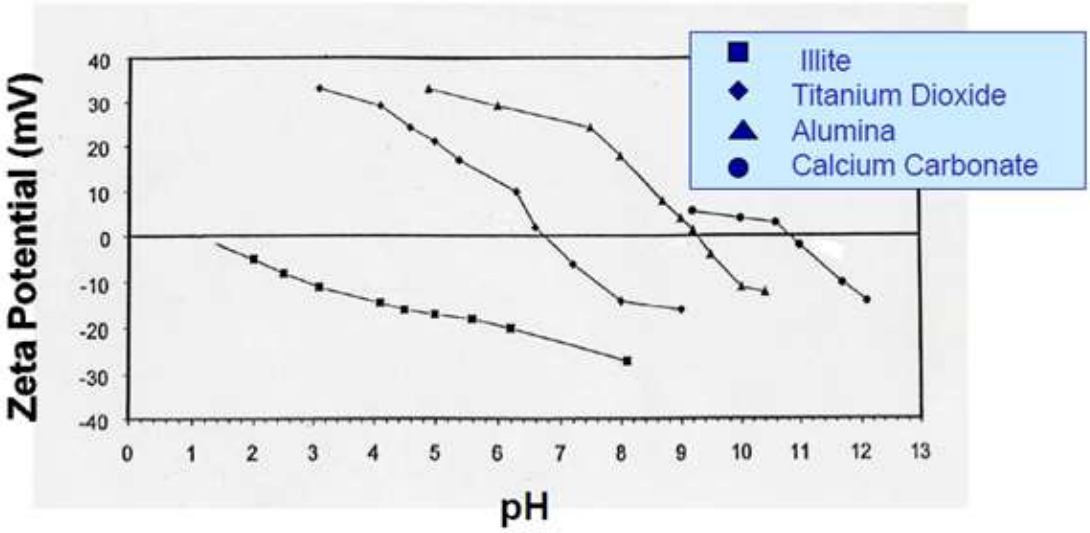

Figure 5. Aqueous Isoelectric points of different materials. It can be seen that the graph of z-ph giving us where the isoelectric points of these materials are. The ISO point can be used on order to characterize these materials and moreover predict their behavior in aqueous fluids [3].

Finally, it is a mistake to assume that the z-potential is not relevant for particles that, at first sight, do not appear to carry a charge. Non-oxides like silicon carbide and silicon nitride are used as abrasives. Their fundamental surface chemistry would normally render

the materials hydrophobic. However, because of surface impurities and contamination they can develop a charge in aqueous solution even to the point of exhibiting an IEP.

1.5 Influence of the environment to the z-potential

As it was further developed the z-potential is calculated in realation to the debuy-Huckel parametrer that in its turn depends on several environmental conditions. In the following bullets the most importa conditions are decribed and brief exaplanations of the z-potential dependacy of each parameter is given.

1) pH In aqueous media

The pH of the sample is one of the most important factors that affects its zeta potential. A zeta potential value on its own without defining the solution conditions is a virtually meaningless number. Imagine a particle in suspension with a negative zeta potential. If more alkali is added to this suspension then the particles tend to acquire more negative charge. If acid is added to this suspension then a point will be reached where the charge will be neutralised. Further addition of acid will cause a build up of positive charge. Therefore a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH. There may be a point where the plot passes through zero zeta potential. This point is called the isoelectric point and is very important from a practical consideration. It is normally the point where the colloidal system is least stable. A typical plot of zeta potential versus pH is shown in figure 8. In this example, the isoelectric point of the sample is at approximately pH 5.5. In addition, the plot can be used to predict that the sample should be stable at pH values less than 4 (sufficient positive charge is present) and greater than pH 7.5 (sufficient negative charge is present). Problems with dispersion stability would be expected at pH values between 4 and 7.5 as the zeta potential values are between +30 and -30mV. According to these behaviors it is expected that above the point of ‘’saturation ‘’ of the double layer a plateau will be exibited showing the stability of the system.

2) Conductivity

The thickness of the double layer (κ^{-1}) depends upon the concentration of ions in solution and can be calculated from the ionic strength of the medium. The higher the ionic strength, the more compressed the double layer becomes. The valency of the ions will also influence double layer thickness. A trivalent ion such as Al^{3+} will compress the double layer to a greater extent in comparison with a monovalent ion such as Na^{+} . Inorganic ions can interact with charged surfaces in one of two distinct ways (i) non-specific ion adsorption where they have no effect on the isoelectric point. (ii) specific ion adsorption, which will lead to a change in the value of the isoelectric point. The specific adsorption of ions onto a particle surface, even at low concentrations, can have a dramatic effect on the zeta potential of the particle dispersion. In some cases, specific ion adsorption can lead to charge reversal of the surface.

3) Temperature

As it was alaso stated in the previous devellopement of the double layer model the thikness of the double layer also depends on the temperature. It is generally accepted that an increase of the temperature will affect the thermal movement of the ions leading to changes in the double layer. Z-potential depends directly to th temperature,as well as indirectly through the known temperature dependence of the dielectric constant of the electrolyte solution and the temperature dependence of the surface equilibrium constants. In the negative charge surfaces an increase of the temperature shows an increase of the z-potential as well.

Chapter 2: Experimental Part

2.1 Experimental Setup

2.1.1 The experimental set up

The experiments designed for this thesis were conducted with the help of the Zeta-Cad meter as shown below at figure 6. It is situated in the laboratory facilities of the ENSIACET . The machine was installed in the lab during 2009 and since then it has only been used by a PhD student as a complementary characterization method.

Figure 6.A close view of the Zeta-Cad from the front. On the right side it can be observed the vessels that contain the electrolyte .These containers are installed on the left side of the Zeta-Cad while operating. On the front side it can be seen the place where the cellule is placed with the two electrodes being on the left and right side of it.

The Zeta-Cad presented in the previous figure 6 is a machine designed in order to study colloidal properties and surface charge of the particles and flat surfaces. The basic principle of the Zeta-Cad has been explained on the chapter concerning the streaming potential that arises when a liquid flows through a channel made by two parallel surfaces.

The machine forces the liquid to flow under a certain Δp value and at the same time it measures the streaming potential along the channel. The streaming potential is measured

by the existence of two electrodes just before the entrance and just after the exit of the channel.
The diagram below describes the measuring principle:

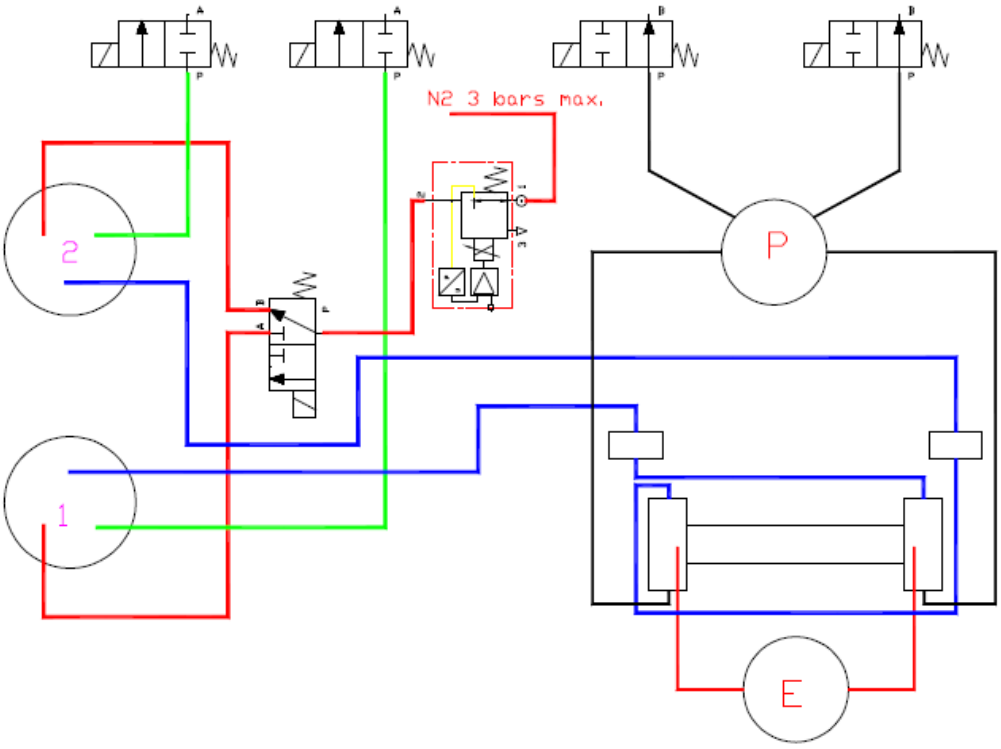

Figure 7. Plan of the liquid flow inside the machine.1,3 are the containers. Blue line leads to the cell and the red one connects the containers. The green line is for purging the system and leads the flow to a waste container behind the machine.

As it can be seen in figure 7, the electrolyte in containers 1 and 2 flows back and forth through the porous plug controlled by the pressure applied using nitrogen gas. The direction of the flow is controlled by a 3-outlet valve and air pressure valves. The flow is controlled by level detectors in the electrolyte containers.

The parameters recorded are the differential pressure (P) the voltage (E) across the c, temperature (T) and electrical conductivity of the solution (λ or K^{σ} as mentioned previously). Variable voltages are measured across the channel tube using different pressure setting. With that procedure paired values of Δp and E are obtained which they form a

scatter line and given the value of the slope through eq. 19 the z-potential is measured.

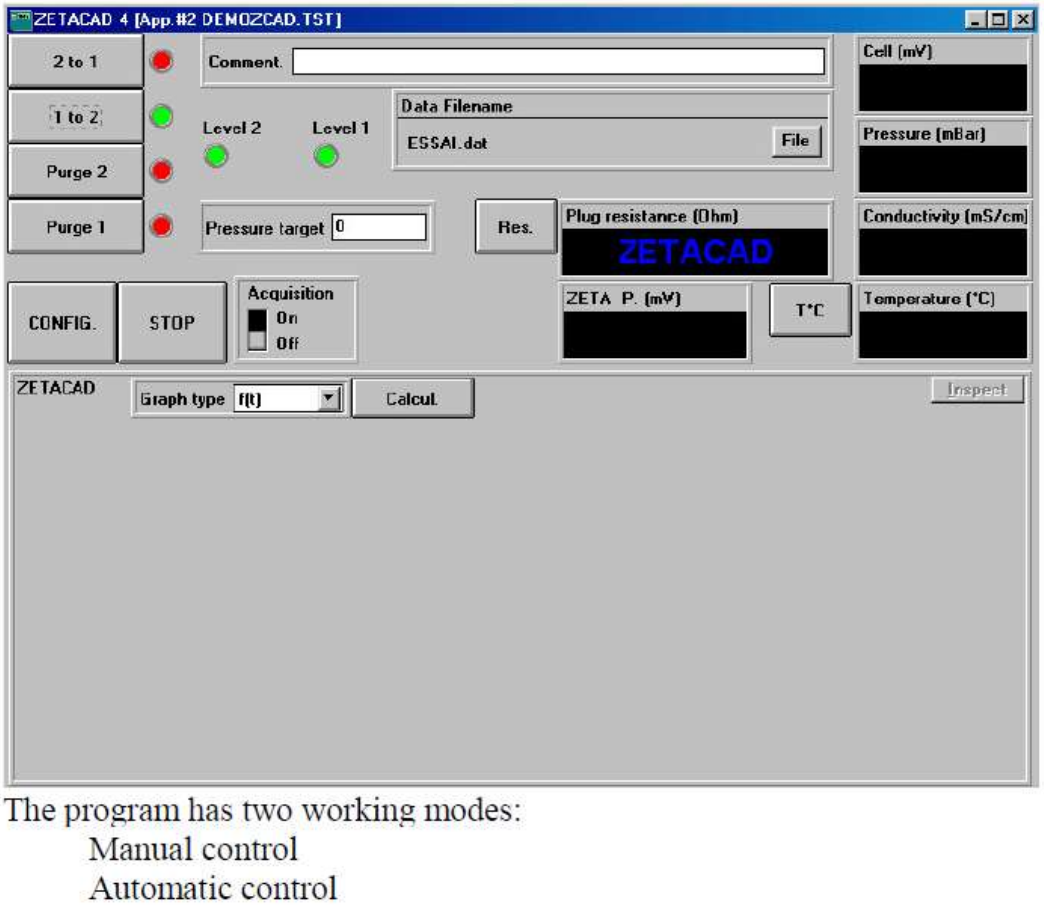

Figure 8. The working environment of the software of the Zeta-Cad as described previously.

The instrument is controlled by a computer programme with the following parameters: pressure to apply length of time to maintain pressure, increments by which to increase pressure. The instrument is designed to work automatically based on the input given, however it can also be controlled manually.

2.1.2 Cell

The cell is the heart of the measurement since all the phenomena are developed there. The Zeta-Cad is designed is such a way that cells of different dimensions and for different materials can be used. In our lab where the surface of flat materials is the key point a special cell is used and it is described accordingly.

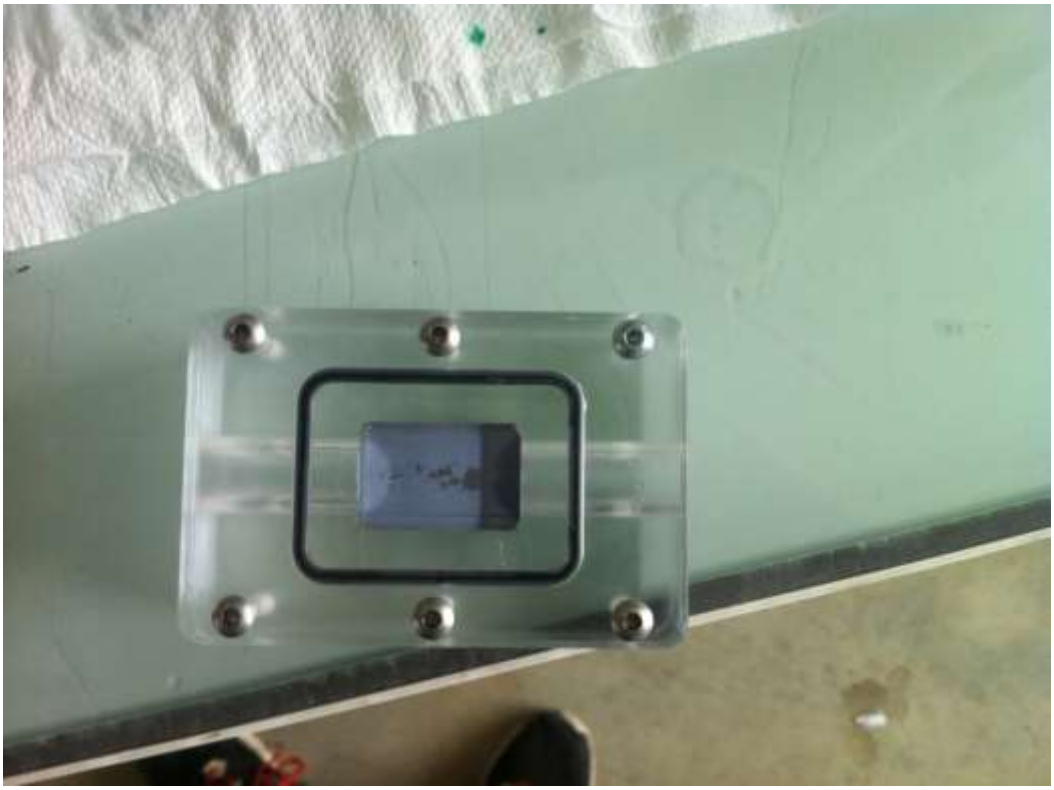

Figure 9. The cell of the Zeta-Cad with the samples already installed.

The cell used is designed to create a parallel channel between 20 and 100µm depending on the thickness of the sample. A laminar flow must be applied during the measurement so a smaller gap beyween the two surfaces will tent to deviate from linearity response. The dimensions of the cell chamber are 20mm in width and 30mm long. After installing the samples the channel created is 15mm in width 30mm long and its height depend on the thickness of the samples used.In this thesis the height was measured to be 0.7mm. In this cell on the first palte is introduced on the bottom. Then two polymer strips are added parallel to each other and to the flow on the two edges of the cell in order to help creat the channel. Finally the second plate is placed on top and the cell is secured with the screws.

The corners are rounded and therefore samples must be carefully designed to fit the cell.

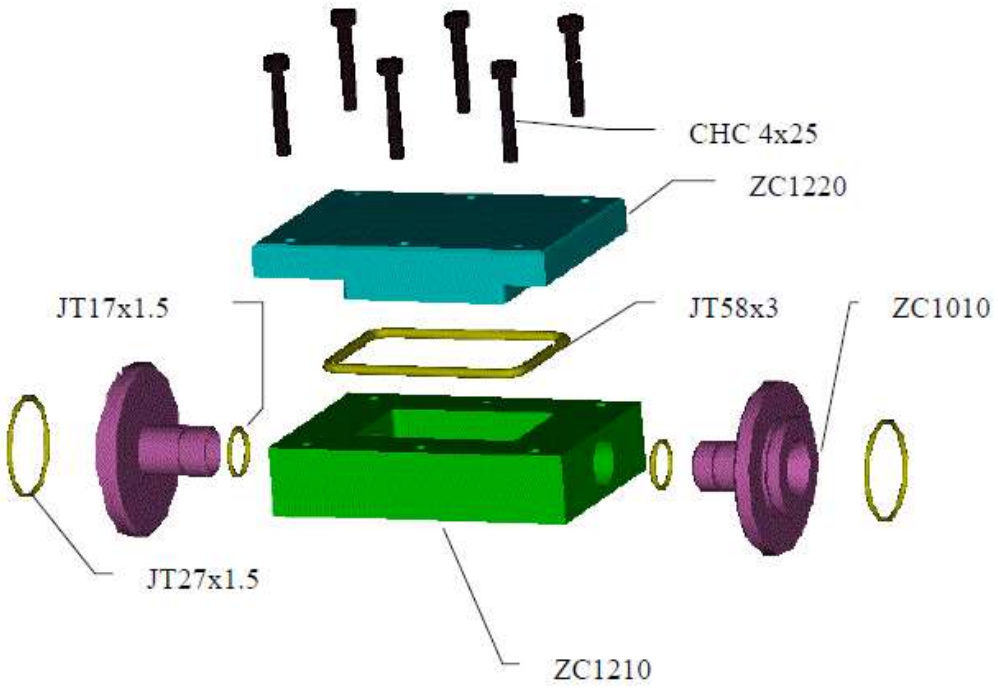

Figure 10. A 3D display of the cell. The plates are put inside the cell (green) and the flow passes horizontally from the 2 purple entrances through the channel.

2.2 Experimental Conditions

2.2.1 Determination of z-potential

The experiements conducted were separated in two defferent series, . The main purpose was to measure the z-potential of SiO_2 plates in different pH.

The samples used were plates of SiO_2 of native oxide elaborated with the Czeochralski method. The thickness of the plates was measured in the lab and it was found to be 0.48μm +/- 0,05μm. The channel was formed by using 2 Teflon lines which were situated on each side of the plate in order to form the streaming channel. The dimensions of the channel are 15mmX30mm .The pressure drop *(Δp)* across the ends of the channel was monitored by the machine automatically. The streaming potential was automatically measured by the two electrodes situated on the sides of the cell. These electrodes were reversible Ag/AgCl and the last time that has been renewed is unknown. The pH of the solution was measured with a cyberScan pH/ion 510 pH meter, following the ISO 9001, each time calibrated with reference samples solutions of 4.01 and 10.01pH. The temperature and the conductivity was measured automatically by the machine and displayed on the software screen.

Each measurement sequence consists of adjusting the pH of the electrolyte solutions, adjusting the vessels, and applying alternating pressure. Both pressure and streaming potential measurements as a function of time are recorded on a computer automatically by the software. The alternating pressure is progressively increased during each measurement sequence; a typical sequence is 5, 10, and 15 (as described further in the protocol, annex B) alternating peak pressure amplitude . At the end of each measurement sequence, the pH of the solution is measured. The temperature is recorded as well, and was typically 21° +/-3° C.

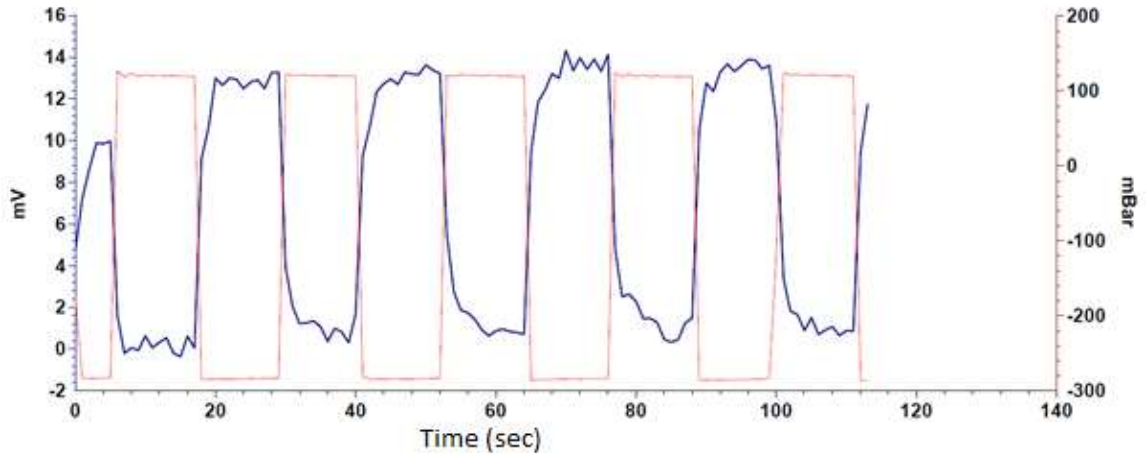

Figure 11. A typical sequence of values while the machine is automatic mode. The blue line presents the streaming potential values and the red represents the applied Δp.

The electrolyte solutions used were aqueous solutions of KCl at concentrations of 10^{-3}M , KCl was chosen because it is a typical electrolyte used in testing devices and also it was the same environment used by the last user. To stabilize the pH of these solutions, buffers were added, namely KNO_3 of 0.1M concentration and H_2SO_4 also at 0.1M.Solutions were prepared with 18 M~-cm deionized water which was previously purified by filtering. CIG high purity grade **(>99%)** nitrogen gas was used for streaming potential measurements and degassing of solution. The laboratory glassware and other vessels used were cleaned and rinsed with deionized water before and after each use and dried in an oven.

The permittivity of vacuum is a build in value in the software as $8.85*10^{-12}Fm^{-1}$

The phenomenological law for the dielectric constant of water (the relative permittivity) is the following:

$$E=0,00073065*T^2*0,39626*T\alpha+87,861$$

And for water viscosity in Pa*s is

$$\eta=1,71E\text{-}07*T^4\text{-}2,29*10^{-5}*T^3+1,44^{E}\text{-}03*T^2\text{-}6,03*10^{-2}*T\alpha+1,787$$

More experiments were conducted based on the protocol previously described with only difference being the electrolyte concetraton and pH of the buffer solution.
The experiments conducted and there conditions are summed up in the following chart:

Experiments	Sample	Value measured	pH	Electrolyte used	Electrolyte concentration
1series of exepements	SiO_2	ζ		KCl	0,001 M
1	SiO_2	ζ	5,9	KCl	0,001 M
2	SiO_2	ζ	7,5	KCl	0,001 M
3	SiO_2	ζ	3,22	KCl	0,001 M
2nd series of experiments			Range of pH		
1	SiO_2	ζ	3,2-10,8	KCl	0,1 M
2	SiO_2	ζ	3,2-11,1	KCl	0,01 M
3	SiO_2	ζ	3,1-9,2	KCl	0,001 M

Table 2. Experiments conducted along with the key conditions (pH, electrolyte and concetration)

Protocol followed

The protocol followed was the one already existing with some light alternations that were considered important for better measurements. The full details of the protocol used can be seen on the appendix B.

After the results of the previous experiment were obtained it was clear that the investigation of silica plates has proven to be more complex than expected. Due to unexplained behavior of the measurments, meaning that instead of obtaining negative values, the experiments gave positive values of z-potential.This lead to further investigation of the silica-liquid interface was needed. As long as the mechanism are investigated and further understood then a better image of the potential of the machine and its usefulness could be established.

Therefore the second series of experiments were scheduled in order to obtain z-potential measurements of silica plates in different KCl concentrations and even more detailed graph (z-pH) especially where the bend points seem to be. KCl was chosen because it is a 1:1 valence electrolyte and therefore the HS equation is more accurate as it has been explained in previous chapters. Also there is rich bibliography data concerning experiments with this electrolyte therefore it is easier to compare and extracte safer conclusions.

Moreover based on the already obtained data it was understood that the structure of the surface plays an important role on the measurement and the value of z-potential. Given that the silica is a material extensively studied by previous researchers it was decided that a new protocol especially for the silica plates should be made in order for the values obtained to serve as a reference point for future measurements and studies.

In order to achieve that it was decided that a special procedure of surface treatment should be performed before the measurements. The procedures aims in eliminating the SiO_2 coating of the wafers. After leaving the samples in plain air for a specific period of time the development of the new surface layer can be. This is done for homogenity reasons and surface roughness control.

2.2.3 Study of the flow behavior

In order to have a better understanding of the above measurements and to actually be able to define the width of the channel, the flow behavior was monitored to confirm the fundamental assumption that flow in the channel is both laminar and established.
The following protocol was used:

The flow rate was measured at applied pressures of 0-0.35bar.In order to test this assumption one of the containers for the electrolyte used in the Zeta-Cad machine was removed. This permitted the collection of the electrolyte while operating the machine.Under constant pressure the output of the electrolyte was collected for a period of 1min.The navier stokes equetions for a rectangular channel[12] were used in order to perfom the caculations

Conditions

The conditions under which the experiment was performed were the same as above. The temperature was measured to be 23^{o}C and the electrolyte was a 10^{-2}M a aqueous solution of KCl. The glassware used for the volume measurement had an accuracy of +/-0.5 ml.

The width and length of the cell was measured as 2cm x 3 cm +/-0.05m respectively. The error for the volume of the electrolyte collected is considered +/- 1ml.

Moreover the ΔP in the software used appears in a 5units scale ranging from 0-225 and not in actuel units (Pa). Therefore it was taken into consideration that the input pressure of N_2 is 3bars, in order to convert the values provided by the software to actual pressure units.

Chapter 3: Results & Discussion

3.1 Reproductibility/repeatability

In this section the values obtained for the first series of experiments are presented. For each pH value, three values of z-potential were obtained in order to have a better picture of the reproducibility and the repeatability of the measures. The values presented later are the values of z-potential obtained for a specific pair of silica in each pH. Three measurements were made per pair of samples per pH.

In the following measurements in order to answer the question of repeatability and reproducibility the two pairs of samples wered used for taking measurements in the same pH. After that, a new pair of samples was used while using 'old' samples for the same measurements at pH 7.5. The values showed in the table are the average of the ones obtained by the two pairs of samples. The deviation between them was <5% which falls within the limits of statistical error.

The table is the following:

Measurments (mV)/pH	1	2	3	Average ± standard deviation
5,9	-49,1	-50,2	-51,75	-50 ±1.33
7,5	-66.98	-68,76	-67,89	-68,32 5±0.62
3,22	-9,32	-9,54	-9,63	-9,497 ±0.16

Table 3. Values of the new measurments conducted at pH 3.22.

The same remarks made for the last table apply also here. What is important to state is that since the values obtained show that the reproducibility is really good even with different samples and the deviation of the values obtained is rmarginal.

In the following in order to be able to have a better look of the behavior of the silica-liquid interface the above data will be plotted and in the same chart with the results of the previous PhD student of the lab.

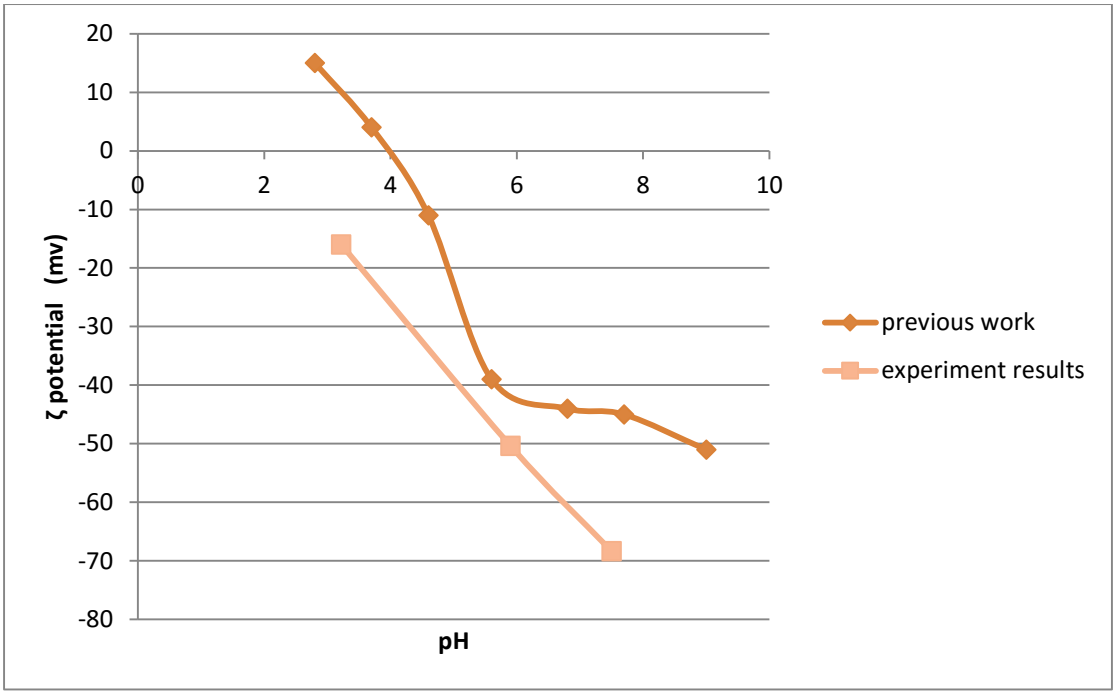

Figure 12. ζ/ pH graph of SiO_2 in a solution of 0,001M KCl in comparison to the expirements findings and previous work [31]

The information given from this graph is that the general tendency of the z-potential being decreased by increasing of the pH of the solution. Also although the turning point where the slope is getting less steep seems to be near the same region (pH 5-6) in the graph of the Phd student a plateau is observed after pH of 7. This is not the case in the line of this thesis experiment where the tendency of the z-potential to decrease after the pH 6 is still observable.

By extending the line of our data in order to cross the X-axis (this was done by plotting a trending line between the first two points for pH 3.22 and 5.9) a isoelectric point at pH 2.66 is obtained. At the same time the line of Simona gives a value of 3.98pH [26]. This is slightly higher than the values reported by Wieset al.[17] for fused silica and Bousse et al for thin film silica but well within the limits of other studies reported by Parks.

Overall this result leads to the assumption that the general motive of the previous experiments is reproduced and that the machine is in a good condition to provide values of z- potential in accordance with the previous references in the bibliography. Nonetheless it is important to observe that although this general reproduction is observed further investigation needs to be made in order to better understand the mechanism of the interface and why there is just a deviation from the values obtained by others. Also a comparison with the already existing data in the bibliography should be made in order to acquire a better image of the machine's accuracy and potentials. Last it is obvious that the data obtained is not enough and in order to make a valid comparison more data and detail is needed while plotting this kind of charts.

In the second series of experiments given the knowledge obtain previously and the new questions that aroused it was attemted to create a richer data chart and through the measurement of z-potential to try and understand how the environment (temperature, concentration, pH) affects the z-potential value. This would help create a frame of how to use and design experiments in this machine in the future.

In the following chart it is presented the findings of another research team of Peter J. Scales, Franz Grieser et Al (1992)[17] since the experimental conditions and goals are similar to this thesis's expiraments. In the following chart it can be seen the z-potential plotted with pH in electrolyte solution of KCl in different concentrations.

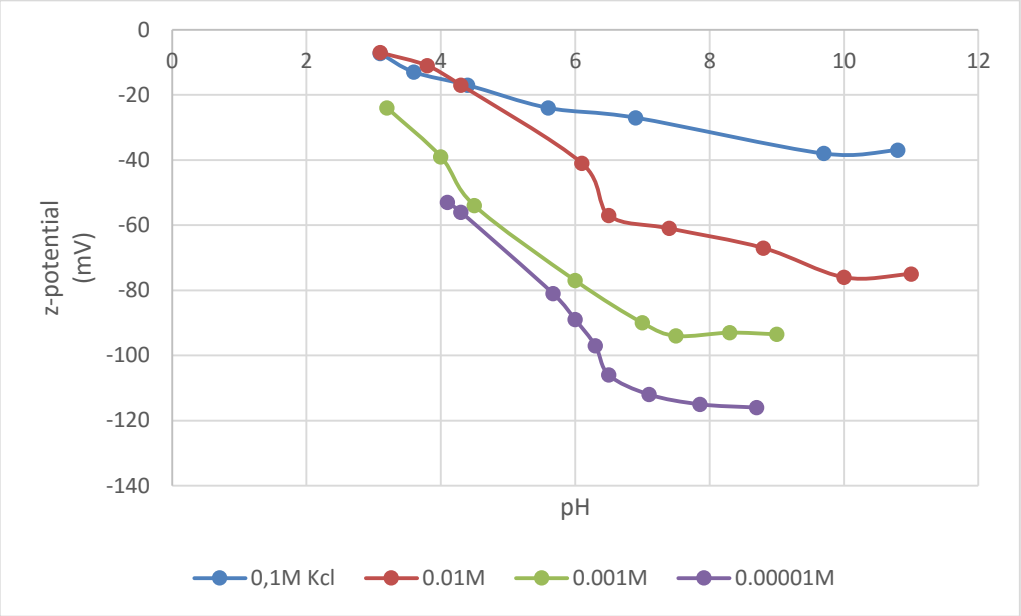

Figure 13. Experimental results along with the values obtained from [19], for similar experiments.

What is important is that the general tendacy of the line is to be linear between the pH of 3-6 and have a turning point at around 7-8 leading to another stable region which seems to be a plateau. These are more obvious for the concentrations of 10^{-2}, 10^{-3} , 10^{-4}M. Moreover all the lines tend to point at the same direction when it comes to low pH. This means that the region where they would cross the X axis is limited between 2-3.5 pH. Therefore no matter the concentration of the electrolyte the isoelectric point seems to be independent and characteristic to each material. As it was stated previously these findings agree with the already bibliography reported.

In the following chart there is the plot of the results from this thesis experiments with the ones obtained by biligraphic reports [19] and also the ones the theoretical model developed in this report, based on the GCSC assumptions. This chart will help understand

the deficiencies of the modeling and the accuracy of our measurements in relation to the theory.

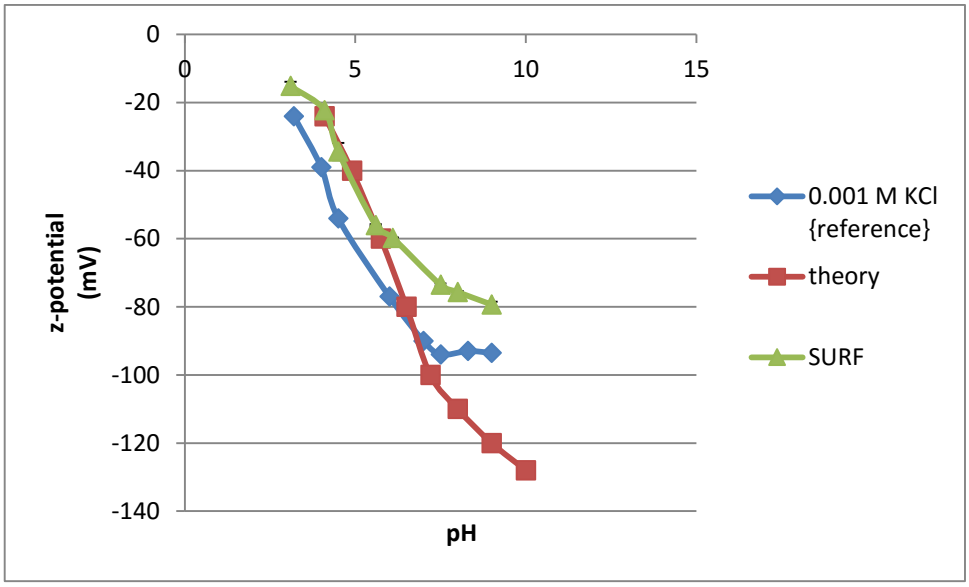

Figure 14. Values of zeta-potential, along with the values obtained from the theoretical models and bilbiographc reports in order to compare their proximity.

The main purpose of the experiments on SiO_2, a very well-studied surface, was to validate the flat-plate method and to increase confidence in the results obtained with it. The magnitude of the z- potential measured is comparable to that found by other investigators. It is about 10 mV more positive than the data obtained by Wiese *et aL (1971)[19]* streaming potentials in vitreous silica capillaries. This means that that the values of these experiments are quite close in comparison to the bibliographic reports.There is also a strong overlap as far as the first part of the lines are concerned pH 3-7 but then there is a strong deviation from theoretical predictions and the experimental data obtained.

Given that the experiments performed in the lab target the establishment of a framework that will help future experimentations planning with more complex material, in the following charts take into consideration the values from other researchers plus the deviation.It has been understood that the z-potential values measured are values that are not static since the equilibrium on the surface of the interface is not static but dynamic which means that the z- potential is constantly changing while in a stable environment. Therefore the line of the charts created is in reality a trend line that passes through a cloud of values of z-potential. This is more obvious if the figure 11 is taken into considerationin which it can be seen that for each pressure value more than one values are obtained.

The protocol that has been created created aims into having a measurement procedure for silica that will give results that will be able to be used as reference for future experiments with different materials. Given all that and seeing the average deviation of the values the following chart was plotted. In this chart the error bars represent the magnitude of the dispersion of the values of z-potential.

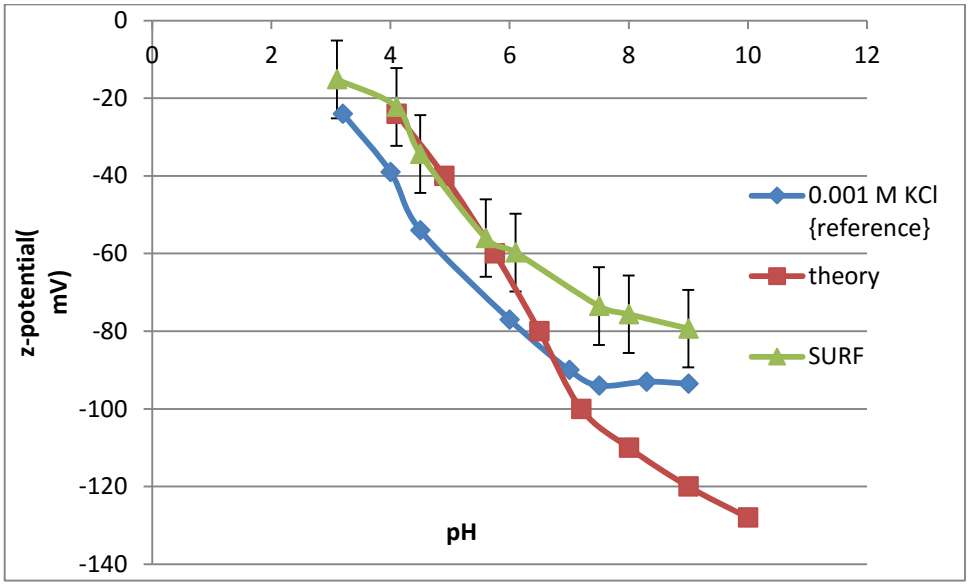

Figure 15. Chart of measurmetns fs z-potential at different pH. The experimental values also have an error bar adjusted taking into consideration the non static nature of the z-potential.

3.3 Flow modeling

In this experiments it was attemted to monitor and verify that the flow behavior inside the cell is as originally assumed while using the HS formula in order to tackle the question of trusting the z-potential measurments raised in the previous discussion. In order to do that it was decided to calculate the Reynolds number inside the cell. After collecting the measurements concerning the flow volume the kinematic viscosity was calculated by the software and furthermore the hydraulic distance it was also calculated for the rectangular channel using the bibliographic formula :

$$D_h = \frac{2(w*l)}{(w+l)} \qquad [24]$$

The table of experiments and further calculations can be seen here:

Number of Exp.	Volume (ml)	Indication	ΔP(bar)	Dp(pascal)	Q(ml/sec)
1	43	5	0,0588	5880	0,71666667
2	88	10	0,1176	11760	1,46666667
3	129	15	0,1764	17640	2,15
4	168	20	0,2352	23520	2,8
5	196	25	0,294	29400	3,26666667
6	236	30	0,3528	35280	3,93333333

Table 4. Measumermnets of volume and other key values are presented in order to estimate the flow rate in the channel.

With this input the Reynolds number can now be calculated and check if it can guarantee a laminar flow, it is reminded that a Re<2000 shows a non-turbulent flow.
In the following table the Reynolds number for each experiment is displayed:

Number of Exp	u(m/s)	Re
1	0,00119444	2,85525E-05
2	0,00244444	5,84329E-05
3	0,00358333	8,56574E-05
4	0,00466667	0,000111554
5	0,00544444	0,000130146
6	0,00655556	0,000156707

Table 5.Reynolds number based on the calculations used for the channel.

With this in mind, the appropriate hydrodynamic equations can be developed and calculate the average fluid velocity ***(u)*** and flow rate **(Q).** For a rectangular channel of length l in the **y** direction, width ***w*** in the x-direction, and height h in the z-direction, it can be shown [19] that the fluid velocity profile in the y-direction through the channel is given by:

And the flow is given by:

$$Q=\frac{w\,h^3\Delta P}{12\eta l}\left[1-\frac{192h}{\pi^5 w}\,tanh\left(\frac{\Pi w}{2h}\right)\right]^{-1} \qquad [25]$$

Having these equations calculations can be made of the flow based on theoretical data. In the lab he have measure the height of the cell formed to be 0.13mm +/-0.01mm. This is a measurement made by in the lab, there are more calculations to be done if needed by using the hagen-poissel formula and solve it for H, but this requires a specific software since analytical methods cannot be applied for solving this equation.

Proceeding, the theoretical values and experimental values of the flow with the differential pressure have been plotted. The experimental results are very close to the theoretical ones and it can be easily conducted that the flow behavior is as assumed laminar and established.

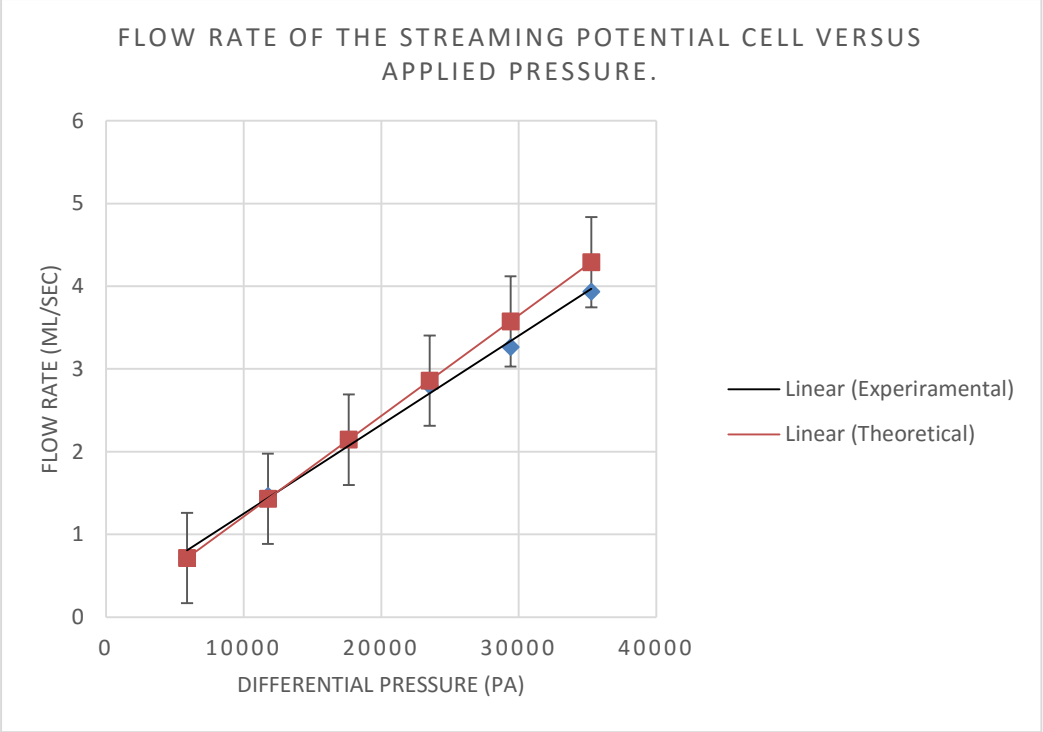

Figure 16. Experimental along with the values theoreticaly predicted for the flow rate of the channel.

3.3 Substrate preparation

Given the need for further elaboration of the z-potential results in order to estimate the trust of these results a new methode of surface treatment before the measruments was introduced. The idea of pre-treating the surfaces was based in the fact that the interfacial chemistry and phenomena are directly affected by the homogeneity and chemistry of the substrate surface. Z-potential is highly sensible to any kind of impurity. In order to tackle this it was decided to treat the SiO_2 surface with HF following the PIRANHA protocol.

The cleaning procedure must be followed called PIRANHA. HF was used in order to remove the SiO2 layer on the surface of the wafer and create a new layer of about 5 Armstrong length. After the procedure was completed leaving the wafer in the air for 20 minutes and then immerse it in (low concentration) of the electrolyte solution to be used for the measurements in order to protect the new layer.

The aim of the whole preparation was to eliminate any impurities and secure the reprudicability of z-potential measurments under the same conditions. This procedure helped in building trust of the results obtained as well as to create a new protocol based on the previous findings in order to use SiO_2 z-potential measurments as a reference point for calibration of the Zeta-Cad machine for future measuerments.

3.4 Discussion

In the previous chapter the experimental data were presented while there was also a compariston with bibliographic data. Although an experimental approach of the z-potential was attemted in order to investigate its potential as a characterization technique, it would

be useless to use these results if the theoretical aspect of the silica liquid interface was not also considered. So in this part is an attempt to combine the theory that has been described in the theoretical part with the experimental results since it is the only way to explain and predict the behavior of the these kind of systems (solid/liquid interface). This kind of investigation will give some interesting results plus will help to better understand the Zeta-Cad machine.

The base of understanding the behavior of the system is the model of the double layer that it will be used. The GCSC model is the most common but it is not applicable for every system and it has its limitations. The full development of the models and direct assignment to the physical properties would be the most accurate approach but this exceeds the purpose of this study, where the practical issues are to be tackled efficiently by the combination of experience and theory. According to the analysis and to the bibliography this model tends to underestimate the values of z-potential and this is because it fails to take into consideration that the capacitance of the surface is not stable but depends on the surface potential. This is why this deviation from pH 7 and higher between theory and experiment data is observed. The capacitance represents the surface density charge in the OHL which is quite dependent on the environment and the specific absorption of ions. Other researchers [13] have made it possible to take into consideration this factor getting better agreement with experimental and theoretical results.

Furthermore in order to better understand the phenomena the interfacial chemistry should be taken into consideration. Knowing that the silanol groups (Si-OH) that exist in the surface behave as fable acids explains why the surface is charged negatively and why it is really difficult to obtain positive values of z-potential. Only in an extremely acid environment the H^+ would be in such a concentration and would have the energy to be absorbed in surface of the silica. Going to the other side of the graph it can be seen that after the pH of 7 there is a plateau forming especially in low concentrations. This is explained by considering that by having higher pH, the absorption of the ions is greater and easier since the energy difference (between the bulk liquid and the surface interface is greater). The existence of the plateau indicates optimum dosage and for stable DL means that the double layer thickness remains unchanged. Practically this tells us the optimum dosage of ions for a stable dispersion.

As far as the behavior is concerned in different concentration it is easy to understand that different concentrations of electrolyte means different ionic strengths of the solution which directly influences the thickness of the double layer(k Debuy-Huckel parameter). As it can be seen from eq [3] increase of the ionic strength compresses the DL giving higher z-potential values (z-potential is depending on the distance from the surface). Therefore this is why the movement of the lines is practically vertically when concentrations are changed. It would be really interesting to investigate further this influence by plotting charts of z-potential/electrolyte concentration.

Even deeper understand of the mechanism can give more valuable information concerning the way the interface works in different environments reaching a point where this information can actually help to pick up the best environmental conditions for a specific experiment.

In conclusion what it should be addressed as the most important remarque is what the UIPAC report [17] has recently stated:

Experience demonstrates that different researchers often find different z-potentials for supposedly identical interfaces. Sometimes, the surfaces are not in fact identical: the high specific surface area and surface reactivity of colloidal systems make z very sensitive to even minor amounts of impurities in solution. This can partly explain variations in electro kinetic determinations from one laboratory to another. Alternatively, since ζ is not a directly measurable property, it may be that an inappropriate model has been used to convert the electro kinetic signal into a z-potential. The level of sophistication required (for the model) depends on the situation and on the particular phenomena investigated. The choice of measuring technique and of the theory used depends to a large extent on the purpose of the electro kinetic investigation.

There are instances in which the use of simple models can be justified, even if they do not yield the correct z-potential. For example, if electro kinetic measurements are used as a sort of quality-control tool, one is interested in rapidly (online) detecting modifications in the electrical state of the interface rather than in obtaining accurate z *-potential*s. On the other hand, when the purpose is to compare the calculated values of ζ of system under given conditions using different electro kinetic techniques, it may be essential to find a true z -potential. The same applies to those cases in which z will be used to perform calculations of other physical quantities, such as the Gibbs interaction energy between particles.

Furthermore, there may be situations in which the use of simple theories may be misleading even for simple quality control. For example, there are ranges of z -potential and double-layer thickness for which the electrophoretic mobility does not depend linearly on ζ, as assumed in the simple models. Two samples might have the same true z -potential and quite different mobility's because of their different sizes. The simple theory would lead us to believe that their electrical surface characteristics are different when they are not.

There are a number of facts that influence the accuracy of and that it should be taken into consideration while applying a model. From our study it seems that surface conductivity flow behavior equilibration of samples and surface density charge are the most important.

As far as trusting the results is concerned facts that built trust are excellent reproducibility and repeatability, the control of the assumptions made for the model applied, as well as the comparison of the values obtained with other sources and if not existent with values of surfaces which close chemical composition and behavior. Procedures should be followed as stated and environmental conditions should be as more precised as possible.

Conclusions

- The measuring of z-potential is a really important characterization technique for materials and can give valuable information for the behavior of surfaces in liquid environments.
- The evaluation of z-potential poses problems since although it is a quite easily defined value, there are large deviations for supposedly identical surfaces between the studies of different research groups.

- The z-potential highly depends on the model used in order to describe the DL formed. Different models can be used depending on the quality and the purpose of the z-potential value obtained. Simple models can be used for fast and general characterization of the surface. More complex models are suggested for highly accuracy measures and for academic purposes where electro kinetic mechanisms and phenomena are investigated.
- SiO_2 is a quite investigated surface but still there no reference samples for streaming potential measurements. SiO_2 could serve as one but the different values reported make it harder.
- Zeta-Cad is suitable for acquiring the isoeletric point of materials which seems to be the most useful value for characterizing the surface since it is unique for each material.
- Experiments show good approximation with reported values, taking into consideration the deviation of measurements that was already expected.
- The model used by Zeta-Cad is a simplified model and can mostly serve for fast and quality based characterizations of surfaces. For academic purposes like investigation of the DL alternations experiments should be based on the equation used and the $\Delta p/E$ data should be handled by the adjusted model.
- The values presented in z-potential/pH charts are representative of a cloud of values of ζ since the equilibrium is dynamic on the surface and the DL is not static but constantly changing.
- Future investigations should be held towards the better modeling of the channel taking into consideration the specificities of the machine. Experiments should be conducted in order to connect z-potential and electrolyte concentration and give additional information. Also it is advisable to investigate the role of surface conductivity as it is indicated in the theoretical part. The model developed in this report can be easily applied and give safe values of surface conductivity so that more information can be acquired about the accuracy of measurements from the Zeta-Cad.

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Appendix A: Estimating the Total Charge in the Diffusive Layer

The Poisson-Boltzmann equation can be solved for the total charge in the diffusive layer in a similar manner the way it is done for the semiconductor surface potential. Beginning with :

$$\frac{d^2\psi}{dz^2} = \frac{2\,q\,c_0}{\varepsilon_0\varepsilon_{sol}}\,\sinh\left(\frac{q\psi}{k_{\mathrm{B}}T}\right) \quad . \tag{1}$$

Re-expressing it via the Debye length,

$$\lambda_{\mathrm{D}}^2 = \frac{k_{\mathrm{B}}T\varepsilon_0\varepsilon_{sol}}{2\,q^2\,c_0} \quad , \tag{2}$$

Leads to the following expression:

$$\frac{d^2\psi}{dz^2} = \frac{k_{\mathrm{B}}T}{q\,\lambda_{\mathrm{D}}^2}\,\sinh\left(\frac{q\psi}{k_{\mathrm{B}}T}\right) \quad . \tag{3}$$

This equation can be rewritten by applying the following identity:

$$2\frac{d\psi^2}{dz^2}\,\frac{d\psi}{dz} = \frac{d}{dz}\left(\frac{d\psi}{dz}\right)^2 \quad . \tag{4}$$

Substituting (4) into (3) leads to a first order differential equation:

$$\frac{\mathrm{d}^2\Psi}{\mathrm{dx}^2} = -\frac{1}{2}\frac{1}{\psi}\frac{d}{dz}(\psi')^2 = \frac{(K_BT)\quad sinh\quad (\frac{q\,\psi}{K_BT})}{q\lambda_D^2}$$

$$\frac{d}{dz}(\psi') = \frac{2\,(K_BT)\quad sinh\quad (\frac{q\,\psi}{K_BT})}{q\lambda_D^2}\,\psi' \tag{5}$$

(5) can be solved via separation of variables. Under the condition of a vanishing electric field for $z \longrightarrow \infty$ the following solution can be derived:

$$
\begin{aligned}
(\psi')^2 &= \frac{2\,k_\mathrm{B}T}{q\lambda_\mathrm{D}^2}\int_{-\infty}^{z_0}\psi'\sinh\left(\frac{q\psi}{k_\mathrm{B}T}\right)dz \\
&= \frac{2\,k_\mathrm{B}T}{q\lambda_\mathrm{D}^2}\int_0^{\psi_0}\sinh\left(\frac{q\psi}{k_\mathrm{B}T}\right)d\psi = \frac{2\,(k_\mathrm{B}T)^2}{q^2\lambda_\mathrm{D}^2}\cosh\left(\frac{q\psi}{k_\mathrm{B}T}\right)\Bigg|_0^{\psi_0} \\
&= \frac{2\,(k_\mathrm{B}T)^2}{q^2\lambda_\mathrm{D}^2}\left(\cosh\left(\frac{q\psi_0}{k_\mathrm{B}T}\right)-1\right)
\end{aligned}
\qquad (6)
$$

$$
2\sinh^2(x/2) = \cosh(x) - 1
$$

Exploiting the identity, the expression for $(\psi')^2$ can be formulated as:

$$
(\psi_o')^2 = \frac{4(K_BT)^2\,sinh^2(\frac{q\,\psi}{K_BT})}{q^2\ \ \lambda_D^2} \qquad (7)
$$

In the last calculation step Gauß's law is utilized to express the total charge per unit area in the Gouy-Chapman layer:

$$
\sigma_o = \pm\sqrt{8\varepsilon\varepsilon_o K_B T c_o}\,\sinh(\frac{q\,\psi}{K_BT}) \qquad (8)
$$